An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials

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ABSTRACT

A framework for the evaluation of inorganic constituent leaching from wastes and secondary materials is presented. The framework is based on the measurement of intrinsic leaching properties of the material in conjunction with mathematical modeling to estimate release under field management scenarios. Site-specific and default scenarios are considered, which may be selected based on the evaluation context. A tiered approach is provided to allow the end user to balance between the specificity of the release estimate, the amount of testing knowledge required, *a priori* knowledge, and resources required to complete an evaluation. Detailed test methodologies are provided for a suite of laboratory leaching tests.

Key words: leaching; metals; waste; soil; utilization; beneficial use; secondary materials; disposal; landfill; risk assessment; test methods

INTRODUCTION

LEACHING TESTS are used as tools to estimate the release potential of constituents from waste materials over a range of possible waste management activities, including during recycling or reuse, for assessing the efficacy of waste treatment processes, and after disposal. They may also be used to develop end points for remediation of contaminated soils and the source term for environmental risk characterization. (In this context, "source term" refers to representation of constituent release from a waste or contaminated soil that is used in subsequent fate and transport modeling for exposure evaluation in risk assessment.) The Resource Conservation and Recovery Act (RCRA) requires the USEPA to classify wastes as either hazardous or nonhazardous. In implementing this portion of RCRA, the USEPA asks, "Would this waste pose unacceptable environmental hazards if disposed under a plausible, regulatorily defined, mismanagement scenario?" This scenario typically represents "worst-case" management (i.e., the estimated highest risk, plausible, legal management option), and wastes posing such unacceptable environmental hazards warrant classification and regulation as hazardous wastes. In developing the Toxicity Characteristic regulation (40 CFR 261.24), the USEPA defined the plausible, worst-case mismanagement scenario for evaluating industrial waste as codisposal in a municipal solid waste (MSW) landfill. The assumption of this mismanagement scenario, in turn, resulted in the development of the Extraction Procedure Toxicity test and its successor, the Toxicity Characteristic Leaching Procedure (TCLP; see 45 FR 33084,

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May 19, 1980, and 55 FR 11798, March 29, 1990), which attempts to replicate some key leaching factors typical of MSW landfills.

The TCLP has come under criticism because of over-broad application of the test (and underlying assumption of MSW codisposal) in evaluating and regulating wastes, and some technical specifications of the methodology. The Science Advisory Board of USEPA reviewed the leaching evaluation framework being employed by the agency in 1991 and 1999 (USEPA, 1991, 1999). In the 1999 review, the Science Advisory Board stated:

> The current state of the science supports, even en-courages, the development and use of different leach tests for different applications. To be most scientifically supportable, a leaching protocol should be both accurate and reasonably related to conditions governing leachability under actual waste disposal conditions.

and

> The multiple uses of TCLP may require the devel-opment of multiple leaching tests. The result may be a more flexible, case-specific, tiered testing scheme or a suite of related tests incorporating the most important parameters affecting leaching. Ap-plying the improved procedure(s) to the worst-case scenario likely to be encountered in the field could ameliorate many problems associated with current procedures. Although the Committee recognizes that these modifications may be more cumbersome to implement, this type of protocol would better predict leachability.

The Science Advisory Board also criticized the TCLP protocol on the basis of several technical considerations, including the test's consideration of leaching kinetics, liq-uid-to-solid ratio, pH, potential for colloid formation, par-ticle size reduction, aging, volatile losses, and comingling of the tested material with other wastes (i.e., codisposal).

In response, this paper offers an alternative framework for evaluation of waste leaching potential that responds to many of the criticisms of the TCLP. It provides a tiered, flexible framework capable of incorporating a range of site conditions that affect waste leaching, and so can es-timate leaching potential under conditions more repre-sentative of actual waste management. The paper also ad-dresses practical implementation of the framework in different applications, and an example application of this approach for evaluating alternative treatment processes for mercury contaminated soils is presented in a com-panion paper (Sanchez *et al.*, 2002c). The leach testing

protocols used in the framework also address technical concerns with the TCLP. The test protocols provided here are designed only for application to inorganic species; however, the concepts presented for the integrated frame-work are general, with application to both inorganic and organic species. Applicable test methods for organic species are the subject of future development. Complete technical specifications for the protocols are provided in the Appendix.

IS THE RIGHT QUESTION BEING ASKED?

In evaluating the leaching potential of wastes based on a single, plausible worst-case mismanagement sce-nario via TCLP, the USEPA seeks to provide environ-mental protection for unregulated wastes. However, wastes are managed in many different settings, and un-der a range of conditions that affect waste leaching. The reliance of the USEPA on a single, plausible worst-case, management scenario for leach testing may be generally protective, but often at the cost of over regulation. It has also proven to be inadequately protective in some cases (see discussion of spent aluminum potliner regulation at 62 FR 41005, July 31, 1997, and 62 FR 63458, Decem-ber 1, 1997). Although reliance on a single waste man-agement scenario as the basis for leach testing may sim-plify implementation of RCRA, many of the wastes evaluated using TCLP have little if any possibility of codisposal with MSW; assessment of the release poten-tial of wastes as actually managed is needed to better understand the hazards posed by waste. Neither the TCLP nor any other test performed under a single set of conditions can provide an accurate assessment of waste hazards for all wastes.

From an environmental protection perspective (and setting aside the particular requirements of RCRA), the goal of leaching testing is to answer the question "What is the potential for toxic constituent release from this waste by leaching (and therefore the risk) under the se-lected management option?" For environmentally sound waste management, the following questions result from different perspectives:

1. From the waste generator's perspective—which waste management options are acceptable for a waste?
2. From the waste management facility's perspective—which wastes are suitable for disposal in a specific disposal facility?
3. From the potential end-user's perspective—is this sec-ondary material acceptable for use in commerce (e.g., as a construction material)?

The framework for answering these questions should be consistent across many applications, ranging from multiple waste disposal scenarios to determination of the environmental acceptability of materials that may be subject to leaching (e.g., construction materials). At the same time, the framework should be flexible enough to consider regional and facility-specific differences in factors affecting leaching (e.g., precipitation, facility design). A methodology guideline (ENV 12920, 1996) developed under European standardization initiatives recommends that the management scenario be a central consideration in the testing and evaluation of waste for disposal and beneficial use of secondary materials. This methodology is an extension of the approach in the Building Materials Decree established in The Netherlands (Building Materials Decree, 1995).

The answers to the questions posed above require several interrelated assessments including (a) the release rate and total amount over a defined time interval of potentially hazardous constituents from the waste, (b) attenuation of the constituents of concern as they migrate from the waste, through groundwater, to the receptor being considered, (c) exposure of the receptor, and (d) the toxicity of each specific constituent. Considerable effort has resulted in accurate assessment techniques and data for evaluating contaminant transport through the environment (and attenuation), and toxicity for a large number of constituents.

In contrast to the detailed research on constituent fate, transport, and risk following release, estimation of constituent release by leaching most often assumes (a) the total content present is available for release, or (b) the contaminant concentration in the leachate will be equal to that measured during a single batch extraction and is constant with time (this assumption is often referred to as the "infinite source" assumption), or (c) the fraction of the contaminant extracted during a batch extraction is equal to the fraction that will leach (USEPA, 1986; Goumans *et al.*, 1991). These approaches frequently result in grossly inaccurate estimation of actual release (both over- and underestimation). Inaccurate release estimation, in turn, forces disposal of materials that are suitable for beneficial use, mandates remediation of soils to levels beyond that necessary for environmental protection, unnecessarily depletes disposal capacity, or results in groundwater contamination (if release is underestimated). In addition, treatment processes, that may be proven to reduce the extracted concentration for a regulatory test (TCLP), have resulted in increased release when compared to management scenarios without treatment (Garrabrants, 1998). Thus, methodologies that result in a more accurate estimate of contaminant leaching may both improve environmental protection through

more efficient use of resources and be economically beneficial.

In general, leaching tests can be classified into the following categories (Environment Canada, 1990): (a) tests designed to simulate contaminant release under a specific environmental scenario (e.g., synthetic acid rain leach test or TCLP), (b) sequential chemical extraction tests, or (c) tests which assess fundamental leaching parameters.

Tests that are designed to simulate release under specific environmental scenarios are limited because they most often do not provide information on release under environmental scenarios different from the one being simulated. This type of limitation has led to widespread misuse and misinterpretation of TCLP results. Reliance on simulation-based testing also results in treatment processes that are designed to "pass the test" rather than to improve waste characteristics or reduce leaching under actual use or disposal scenarios. For instance, it is common practice to include waste treatment additives to buffer the TCLP leachant at a pH resulting in minimum release of target constituents. However, when the buffered material is landfilled, the landfill leachate pH may be dominated either by the material buffering capacity (monofill scenarios) or by other sources (codisposal scenarios). In either case, the release scenario may differ significantly from conditions simulated by the testing protocol, and unpredicted leaching behavior may occur.

Sequential chemical extraction tests evaluate release based on extraction of the waste with a series of increasingly more aggressive extractants. The sequential extraction approach, originally compiled by Tessier *et al.* (1979), has been adapted by others (Frazer and Lum, 1983). These adapted approaches have limitations that require case-by-case evaluation (Khebohian and Bauer, 1987; Nirel and Morel, 1990). In addition, the operationally defined nature of sequential extraction approaches make generalized application in a waste management framework difficult.

In addition, geochemical speciation modeling also can provide useful insights into leaching behavior, as it provides information on possible solubility controlling mineral phases (Meima *et al.*, 1999; van der Sloot, 1999; Crannell *et al.*, 2000), the role of sorption processes with Fe, Mn, and Al phases (Meima and Comans, 1998, 1999), and complexation with dissolved organic matter (Keizer and van Riemsdijk, 1998; Kinniburgh *et al.*, 1999; van der Sloot, personal communication 2002). However, geochemical modeling often requires detailed solid phase identification that is either impractical or not possible for complex materials, and needed solubility and adsorption parameters may be unavailable. Although the information it provides can be used effectively in waste man-

agement, geochemical modeling often only provides qualitative or semiquantitative results, and is not a tool for regulatory control.

The alternative framework described below was designed to assess intrinsic waste leaching parameters, thereby providing a sound basis for estimation of release potential in a range of different potential waste management scenarios. It provides a basis either for choosing acceptable management or disposal from among several possible options or for judging whether a preselected management or disposal option, is, in fact, environmentally sound and appropriate.

AN ALTERNATIVE FRAMEWORK FOR EVALUATION OF LEACHING

Waste testing should provide information about potential contaminant release from a waste in the context of the anticipated disposal or utilization conditions. Thus, testing should reflect the range of conditions (e.g., pH, water contact, etc.) that will be present in the waste and at its interface with its surroundings during the long term, which may be significantly different than the properties of the material immediately following production. [Examples where the material as produced has different constituent release behavior than that during utilization are: (1) concrete pillars immersed in surface water where release reflects the neutral pH of surface water rather than the alkali pH of Portland cement concrete (van der Sloot, 2000); (2) stabilized coal fly ash exposed to seawater showing surface sealing (Hockley and van der Sloot, 1991); (3) MSWI bottom ash used in road-base application being neutralized with a few years of field exposure (Schreurs *et al.*, 2000); and (4) use of steel slag in coastal protection applications where V and Cr leaching is reduced by the natural formation of ferric oxide coatings in the utilization environment (Comans *et al.*, 1991).]

The goals of a revised framework for evaluation of contaminant leaching should be to: (a) provide conservative (in this paper, "conservative" estimates of release implies that the actual release will be less than or equal to the estimated release during the management scenario considered.), but realistic estimates of contaminant leaching for a broad range of waste types, constituents of concern, environmental conditions, and management options; (b) utilize testing strategies that can be carried out using standard laboratory practices in reasonable time frames (e.g., several hours to several days, depending on requirements); (c) provide for release estimates that consider site-specific conditions; (d) encourage improvements in waste management practices; (e) provide flexibility to allow level of evaluation (and hence degree of overconservatism) to be based on the user's requirements; (f) evolve in response to new information and take advantage of prior information; and (g) be cost effective. (For most cases, more detailed waste characterization results in more accurate estimates of actual contaminant release, providing safety margins by reducing the degree of overestimated release. However, more detailed characterization requires additional testing cost and time, which may not be justified because of either the limited amount of waste to be managed, time constraints, or other reasons.)

In concert with these goals, evaluation of constituent release can be approached by a series of steps: (1) define management scenarios and mechanisms occurring in the scenarios (e.g., rainfall infiltration) that control constituent release; (2) measure intrinsic leaching parameters for the waste or material being evaluated (over a range of leaching conditions); (3) use release models incorporating measured leaching parameters (corresponding to anticipated management conditions) to estimate release fluxes and long-term cumulative release; and (4) compare release estimates to acceptance criteria. Management scenarios can either be default scenarios that are designed to be conservative or incorporate site-specific information to provide more accurate estimates of release. In CEN TC 292, such a scenario-based approach has been described as an experimental standard (ENV 12920, 1996). This standard describes steps very similar to those identified above. [CEN/TC 292 is the European Standardization Organization (CEN) technical committee dealing with characterization of waste (established in 1993). For additional information, see www.cenorm.be on the Internet.]

The controlling release mechanisms most often can be described in terms of either equilibrium controlled or mass-transfer rate controlled. Equilibrium controlled release occurs for slow percolation through porous or granular materials. Mass transfer rate controlled release occurs when flow is predominantly at the exterior boundary of monolithic materials or percolation is very rapid relative to mass transfer rate of constituent release to the percolating water. Intrinsic leaching parameters that are to be measured using laboratory testing are: constituent availability, constituent partitioning at equilibrium between aqueous and solid phases as a function of pH and liquid-to-solid (LS) ratio, acid and base neutralization capacities (ANC and BNC), and constituent mass transfer rates. Definition of management scenarios and application of intrinsic parameters, release models and decision criteria are discussed in later sections of this paper.

To achieve the desired framework goals and series of evaluation steps, a three-tiered testing program is proposed (Fig. 1). An analogous, tiered approach, developed

Figure 1. Alternative framework for evaluation of leaching.
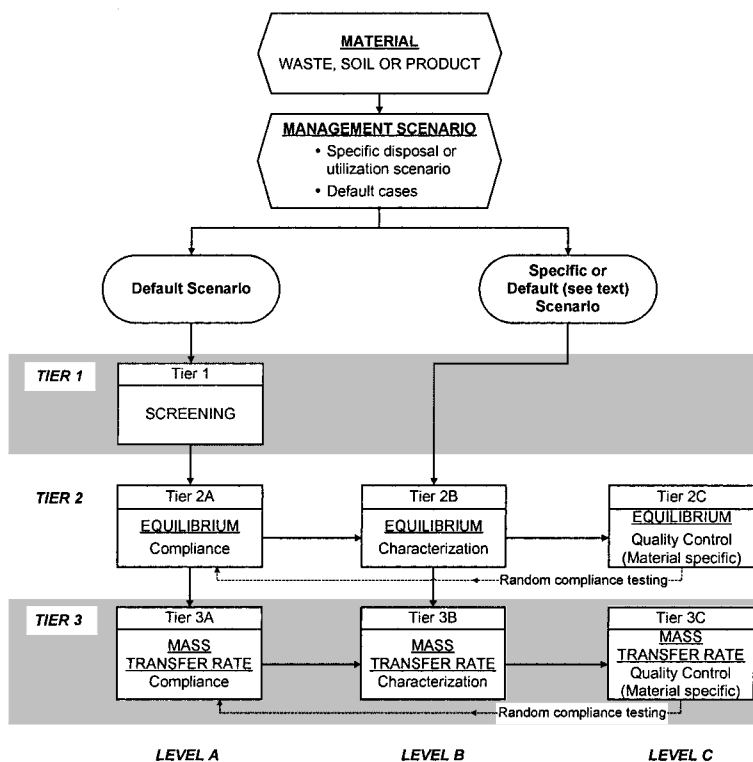
with input from the authors of this paper, has been recommended by Eighmy and Chesner for evaluation of secondary materials for use in highway construction (Eighmy and Chesner, 2001). In the framework presented in this paper, each successive tier provides leaching data that is more specific to the material being tested and possible leaching conditions than the previous tier. Individual leaching tests are designed to provide data on intrinsic leaching parameters for a waste or secondary material. Results from multiple tests, used in combination with either default management scenario assumptions (more conservative, but with simpler implementation) or site-specific information, provide more accurate release assessments. However, the results of a single test (e.g., the first tier availability test) can be used as the most conservative approach for management decisions when time or economic considerations do not justify more detailed evaluations.

Three tiers of assessment can be defined to efficiently address the above waste management questions and criteria: Tier 1—screening based assessment (availability); Tier 2—equilibrium based assessment (over a range of pH and LS conditions); and Tier 3—Mass transfer based assessment.

Progressing from Tier 1 through Tier 3 provides increasingly more realistic and tailored, and less conserv-

ative, estimates of release, but also requires more extensive testing.

Tier 1 is a screening test that provides an assessment of the maximum potential for release under the limits of anticipated environmental conditions, without consideration of the time frame for release to occur. This concept of maximum potential release is often referred to as "availability." In practical application, availability is operationally defined using a selected test method. Leaching potential is expressed on a mass basis (e.g., mg X leached/kg waste). The basis for this bounding analysis would be testing under extraction conditions that maximize release within practical considerations (see further discussion below). Tier 2 testing is based on defining liquid–solid equilibrium as a function of pH and LS (i.e., chemical retention in the matrix). Tier 3 testing uses information on liquid–solid equilibrium in conjunction with mass transfer rate information (i.e., physical retention of constituents in addition to chemical retention in the matrix). Both Tier 2 and Tier 3 testing may use either default or site-specific management assumptions (e.g., infiltration rates, fill depth) to estimate release as a function of time. For a scenario, leachate concentrations based on equilibrium will always be greater than or equal to those based on mass transfer rate. Thus, equilibrium release estimates (Tier 2) may be a conservative approximation in

the absence of mass transfer rate information (Tier 3). (Extrapolation of laboratory mass transfer tests results to field conditions requires careful consideration of the external surface area for water contact and the potential for external stresses.)

For Tier 2 and Tier 3 assessments, three levels of testing (Levels A, B, or C) are defined. Each of the three levels of testing may be used, depending on the amount of previous knowledge (test data) of the waste, or the degree of site-specific tailoring desired. Level A (in either Tier 2 or 3) uses concise or simplified tests. The basis for Tier 2A would be measurement of the leaching characteristics at conditions that bound the range of anticipated field scenarios for equilibrium (e.g., use of three extractions to define release at acidic, neutral, and alkali pH conditions with consideration of the material's natural pH at LS = 10 mL/g). The basis for Tier 3A testing would be a coarse estimate of release rates (e.g., a four-point, 5-day monolithic leach test). The data from these tests would be used in conjunction with default management scenario bounding conditions, and simplified release models, to provide a conservative assessment in the absence of more detailed knowledge. Example applications of Level A testing (in either Tier 2 or 3) include for routine disposal of wastes that may fail Tier 1 testing, simplified evaluations for disposal or utilization that can be justified based on more conservative assumptions, and verification that a material being tested exhibits characteristics similar to a class of materials that has previously been more extensively characterized (e.g., Level B, see below).

Level B testing provides detailed characterization of the waste or secondary raw material. The basis for Tier 2B testing would be definition of equilibrium over the full range of relevant pH and LS conditions (i.e., pH 2–13, and LS 0.5–10 mL/g). The maximum release observed under these conditions also is functionally equivalent to the availability measured in Tier 1, although the specific values may differ based on the method of determination. The basis for Tier 3B testing would be a more complete definition of mass transfer rates (e.g., 10 data points over 60 days) and verification of material integrity (e.g., strength after leaching). These more detailed data can be used in conjunction with either default or site-specific management scenario assumptions, and either simplified or advanced release models. For example, results from Level B testing in conjunction with default scenarios and simplified release models can provide the basis for comparison of treatment processes. Results from Level B testing used in conjunction with site-specific information and advanced models provide the most realistic and least conservative assessment. Level B testing would only be carried out initially for a material or class

of materials generated in large quantities, and thereafter only if significant changes in material characteristics are indicated by periodic Level A testing. Level B testing provides insight into the critical components for a given material, thus providing the basis for selection of a reduced set of parameters for subsequent testing. After completion of Level B testing, Level A testing can be used to answer the question, "Does the material currently being tested have the same characteristics of the material that was previously characterized in more detail (Level B)?" The frequency of testing can be related to the degree of agreement with the level B testing. Good performance is then rewarded by reduction in test frequency. A deviation then requires initially more frequent testing to verify the deviation, and if necessary, a return to the level B testing to evaluate the cause. Additional examples of application of Level B testing include monofill disposal of special wastes and approvals for beneficial use of secondary materials.

Level C provides the most simplified testing for quality control purposes, and relies on measurement of a few key indicators of waste characteristics, as identified in the level B testing. An example of Level C testing would consist of titration of a sample to a designated pH with measurement of the concentration of a limited number of constituents in the resulting single extract. Specific Level C testing requirements would be defined on a case specific basis. Level C should only be used after Level B testing has initially been completed to provide a context for quality control. One application of Level C testing would be the routine (e.g., daily, weekly or monthly) evaluation of incinerator ash prior to disposal.

A feedback loop is provided between Tier 2C and Tier 2A within the framework (Fig. 1). This loop is provided to indicate that Tier 2A testing can be used on a random basis to provide further assurance of attainment of regulatory objectives when much more simplified testing is allowed on a routine basis (Tier 2C). In this case, the Tier 2A testing is compared with the more complete Tier 2B characterization testing to verify that the batch of material being tested has not deviated significantly from the material that was originally characterized, and serves as the baseline assessment. A similar approach may be used when quality control testing is based on mass transfer rate testing (Tier 3C) rather than equilibrium testing (Tier 2C).

Although the above framework provides the specific basis only for evaluation of inorganic constituents, an analogous set of test conditions can be described for evaluation of organic constituents. Additional considerations for organic constituents would include (a) the potential for mobility of a nonaqueous phase liquid, (b) the fact that pH dependence of aqueous partitioning is usually limited to the indirect (although important) effect of pH

on dissolved organic carbon levels from humic or similar substances, and (c) availability for many organic constituents is limited, and may require a more complex modeling approach.

DECISION MAKING BASED ON THE EVALUATION FRAMEWORK

Application of laboratory testing results to environmental decision making requires linking the laboratory data to environmental end points of concern (protection of human health and environment). This is done through data or models that represent environmental processes, including groundwater transport of released constituents, exposure to humans or animals via drinking water, and the toxicity of the released constituents of concern.

This linkage was established for the TCLP based on assuming the test results yielded a leachate constituent concentration that reflected anticipated field leachate that would be produced during disposal in the bounding scenario. This leachate constituent concentration, in turn, would be reduced through natural groundwater attenuation processes as it moved through the groundwater (e.g., dilution and adsorption) before reaching a drinking water well. This "concentration-based approach" implicitly assumes an infinite source of the constituents of concern, and does not account for either the anticipated changes in release over time (including exhaustion of the source) or the potential for cumulative effects of release over time. Furthermore, this approach considers only the leaching behavior of the material; it does not consider the management context (e.g., disposal vs. utilization, design of the management scenario, geographic location). Thus, the concentration-based approach establishes a leachate concentration (as measured in the TCLP), below which no significant impact to drinking water is anticipated. This approach also can be misleading if the test conditions do not reasonably reflect the field conditions (e.g., with respect to pH and LS ratio).

The proposed alternative is a performance or "impact-based approach." This approach focuses on the release flux of potentially toxic constituents over a defined time interval. Thus, the management scenario is evaluated based on a source term that incorporates consideration of system design, net infiltration, and the leaching characteristics of the material. Basing assessment and decisions on estimated release allows consideration of the waste as containing a finite amount of the constituent of interest, the time course of release, and the ability to adapt testing results to a range of management scenarios. The measure of release would be the mass of constituent released per affected area over time (i.e., release flux). Knowl-

edge of the release flux would allow more accurate assessment of impact to water resources (e.g., groundwater or surface water) by defining the mass input of constituent to the receiving body over time. Results of this impact-based approach can provide direct input into subsequent risk assessment for decision making, either based on site-specific analysis or using a generalized set of default assumptions.

Management scenarios

Waste management or utilization scenarios must be used to link laboratory assessment results to impact assessment. Defining scenarios for this purpose requires the leaching mode controlling release (equilibrium or mass transfer), the site-specific LS ratio, the field pH, and a time frame for assessment. Values describing a specific waste management facility or a hypothetical default scenario could be used. Using these site conditions with laboratory measures of constituent solubility as a function of pH and LS ratio, a simple release model can be used to estimate the cumulative mass of the constituent released over the time frame for a percolation/equilibrium scenario. Including laboratory measurement of mass transfer rates allows for application of simple release models for mass transfer rate controlled management scenarios (e.g., monolithic materials).

For a hypothetical default landfill disposal scenario, parameter values may be based on national data for different landfill types, or defined as a policy matter. Values for field pH and LS ratio may be either measured at an actual site or estimated for the site. Measuring field pH requires collecting landfill leachate or landfill pore water and measuring the pH before contact with the air begins to alter the pH. LS ratio serves as the surrogate parameter for time. Good agreement has been obtained between laboratory test data and landfill leachate based on LS (van der Sloot, 2001). Measuring field LS ratio involves measuring the volume of leachate collected (annually) from the landfill, and comparing it with the estimated waste volume in the landfill, or the landfill design capacity. As an alternative to measuring the LS ratio, it may be estimated, based on defining the geometry for the management scenario and local environmental conditions. Parameters for defining the management scenario include fill geometry (relating waste mass to impacted area), net infiltration rates (defining amount of water contact), and time frame. For example, a default disposal scenario may be a fill height of 10 m, 20 cm infiltration per year and 100 years (alternatively, the total mass of waste and footprint area may be specified). The selection of the default management scenario is ultimately a consideration of typical waste management practices and of soci-

etal value judgments reflected in the regulatory development process.

For discussion purposes, a 100-year interval is suggested as a hypothetical assessment period, although other time frames could be used. (The authors have found 100 years to be a useful period for release estimates. This period is typically longer than a lifetime but short enough to be comprehendible. In addition, for many cases, a major fraction of the long-term release is anticipated to occur during a period less than this interval.) For comparison of treated wastes, a cube 1 meter on edge is assumed. Laboratory test results are presented primarily as release per unit mass of waste tested (e.g., mg X/kg waste), but also are presented and used on a concentration basis for Tier 2 testing.

Environmental considerations

Release estimates for most cases assume that conditions influencing release are controlled by the waste material and associated design conditions; however, properties of surrounding materials may dominate the release conditions in some scenarios. These external stresses (e.g., pH or redox gradients, carbonation, comingling effects) can lead to substantial deviation from material-driven leaching behavior. For instance, caution must be used if large pH or redox gradients exist between the waste and the surrounding environment or within the waste matrix. The solubility of many inorganic species may be strongly a function of pH (e.g., Pb, Cd, Ba) or significantly altered by redox conditions (e.g., Cr, Se, As). Large gradients in pH or redox potential can result in precipitation or rapid dissolution phenomena for some elements as concentration gradients within the material or at the material boundary redistribute over long time intervals (van der Sloot *et al*., 1994; Sanchez, 1996). The release of highly soluble species (e.g., Na, K, Cl) is not considered a strong function of leachate conditions.

Redox gradients and reducing conditions may result from material characteristics, biological activity, or external inputs. Materials with inherent reducing properties include several types of industrial slag, fresh sediment, and degrading organic matter. Testing of these materials under air-exposed conditions may lead to unrepresentative answers for the situation to be evaluated. For an appropriate assessment of reducing materials, testing and release modeling that considers conditions imposed by external factors, rather than by the waste itself, will be necessary. This is still an underdeveloped area of research.

For most alkaline wastes, the most prevalent interface reaction is absorption of carbon dioxide. Carbonation of waste materials results in the formation of carbonate species and neutralization of alkaline buffering capacity.

For Portland cement-based matrices, the conversion of calcium hydroxide to calcium carbonate has been noted to reduce pore water pH towards 8 (Garrabrants, 2001; Sanchez, 2002a). Thus, if pH-dependent species are a concern, carbonation of the matrix can play a significant role in predicting long-term release.

Currently, the proposed approach does not consider the impact of comingling different types of wastes during disposal other than the impact of resulting changes in pH. In cases where a pH gradient appears to be the most significant factor, release estimates can be accomplished using advanced modeling approaches in conjunction with characterization data interpolated from the concentration as a function of pH as defined under Tier 2. Test methods and release models to assess the impact of material aging under carbonation and reducing conditions are under development (NVN 7438, 2000; Garrabrants, 2001; Sanchez *et al*., 2001). Experimental work is in progress to evaluate waste–waste interaction by quantifying buffering of pH, dissolved organic carbon, and leaching from waste mixtures (van der Sloot *et al*., 2001a, 2001b).

TEST METHODS FOR USE IN THE FRAMEWORK

Criteria for equilibrium test methods

Important considerations for the design of equilibrium test methods are (a) the relationships between particle size, sample size, and contact time; (b) definition of an appropriate LS ratio; (c) selection of the acid or alkali for pH modification; and (d) practical mechanical limits. Experimental observations with several wastes have indicated that use of a maximum particle size of 2 mm and contact time of 48 h results in a reasonable measurement of equilibrium (Garrabrants, 1998). If diffusion is assumed to be the rate controlling mechanism, the relationships between particle size and contact time required to approach equilibrium can be approximated as diffusion from a sphere into a finite bath (Crank, 1975). Critical parameters are the fraction of constituent released at equilibrium, observed diffusivity, particle diameter, and contact time. The ratio between the fraction of constituent released at a given time and the fraction of the constituent released at equilibrium can be considered an index of the approach to equilibrium. Results of simulations using this modeling approach are consistent with approaching equilibrium after 48 h for observed diffusivities less than 10^{-14} m^2/s (Garrabrants, 1998).

Equilibration times for different particle size systems, assuming all other properties remain constant (e.g., observed diffusivity, liquid–solid ratio, fractional release at

Table 1. Specifications for the base case and suggested alternative conditions for equilibrium extractions.

	Maximum particle size [mm]		
	Base case	*Suggested alternates*	
	2	*0.3*	*5*
Minimum sample size (g)	40	20	80
Minimum contact time (hr)	48	18	168 (7 days)
Container size (mL)	250	500	1,000

equilibrium), can be evaluated using a dimensionless time parameter:

$$\tau = \frac{D^{obs} \cdot t}{r^2} \qquad (1)$$

where τ is the dimensionless time parameter [$-$]; t is the contact time [s]; r is the particle radius [m]; and, D^{obs} is the observed diffusivity [m^2/s].

Based on this approach, achieving a condition equivalent to the 2 mm/48 h case, a particle size of 5 mm would require extraction for 12.5 days; for a particle size of 9 mm, 40.5 days would be required. However, most materials undergoing testing would be sized reduced or naturally have a particle size distribution with the maximum particle size specified. Thus, a maximum particle size of 2 mm with a 48-h minimum contact time is specified as a base case, with alternative conditions suggested considering both equivalent approaches to equilibrium and practical limitations (Table 1). Demonstration of approximating equilibrium conditions for the material being tested is recommended before using alternative contact times.

Selection of sample sizes assumes testing of representative aliquots of the material being evaluated. For the base case with a maximum particle size of 2 mm, a sample size of 40 g (equivalent dry weight) is recommended when carrying out an extraction at an LS ratio of 10 mL/g. Heterogeneous materials and materials with a larger particle size will require either testing of larger aliquots or homogenization and particle size reduction prior to subsampling for testing. A discussion and example of sampling of heterogeneous materials and particle size reduction followed by subsampling for leaching tests is provided elsewhere (IAWG, 1997).

For many test methods, an LS ratio of 10 mL/g has been selected to provide adequate extract volumes for subsequent filtration and analysis while using standard size extraction containers (i.e., 500 mL). This liquid-to-LS ratio also provides for reasonable approach to equilibrium based on theoretical considerations. Typically, use of an LS ratio of 10 mL/g provides solubility-con-

trolled equilibrium over the range of pH relevant for extrapolation to the field. The resulting solution concentration is generally only weakly dependent on LS ratio between LS ratio of 10 and 2 mL/g. LS ratio dependence may be verified using an extraction at lower LS (see methods below).

In the experimental methods, pH adjustments are made using aliquots of nitric acid or potassium hydroxide. Nitric acid was chosen to minimize the potential for precipitation (e.g., such as occurring with sulfuric acid), complexation (e.g., with organic acids or hydrochloric acid), or analytical interferences. It is also recognized that nitric acid is oxidizing, which is a conservative selection due to the solubility behavior of metal hydroxyl species (e.g., $Pb(OH)_3^-$, $Cd(OH)_3^-$) and the potential for oxidizing conditions during management. However, oxyanions (e.g., chromate) exhibit maximum release at near neutral to slightly alkaline conditions that typically are achievable without significant acid additions. Testing for release under reducing conditions requires the development of additional test methods because consideration must be given to acid selection, sample handling, and establishment of reproducible reducing conditions. Potassium hydroxide was selected to avoid interference with the use of sodium ion as an inert tracer in some applications; however, sodium hydroxide may be substituted for cases in which potassium characterization is a concern.

During extraction, complete mixing should be insured by end-over-end mixing. In all cases, it is desired to test the material with the minimum amount of manipulation or modification needed prior to extraction. Thus, it is preferable to avoid sample drying before testing, although this can be acceptable when nonvolatile constituents are of primary interest and it is necessary to achieve particle size reduction.

RECOMMENDED TEST METHODS

The following test methods are recommended for use in the proposed tiered leaching framework. The general

purpose, approach, and application of these test methods are shown in Table 2. Detailed protocols for these test methods are presented as Appendix A.

Tier 1—screening tests

An ideal screening test would result in a conservative estimate of release over the broad range of anticipated environmental conditions. In addition, this screening test would require only a single extraction that could be completed in less than 24 h. However, this ideal scenario is impossible to achieve. Several approaches to measuring "availability" or maximum leaching potential have been developed or considered. One approach is a two step sequential extraction procedure with particle size <300 μm, LS = 100 mL/g and control at pH 8 and 4 (NEN 7341, 1994). Another approach uses EDTA to chelate metals of interest in solution at near neutral pH during a single extraction (Garrabrants and Kosson, 2000). Either of these approaches can be used as a screening test, but both approaches have practical limitations relative to implementation. The NEN 7341 requires a small particle size, two extractions, and pH control. The approach of Garrabrants and Kosson (2000) requires a pretitration, and can have some difficulties in controlling the pH. This approach also has been criticized as providing a release estimate that may be too conservative. (NEN is the national Dutch standardization organization, where a standardization committee has been addressing the development of leaching tests for construction materials and waste materials since 1983. For additional information, see www.nen.nl on the Internet.)

Tier 2—solubility and release as a function of pH

The objectives of this testing is to determine the acid/base titration buffering capacity of the tested material and the liquid–solid partitioning equilibrium of the "constituents of potential concern" (COPCs). For wastes with high levels of COPCs, the liquid–solid partitioning equilibrium is determined by aqueous solubility as a function of pH. For low levels of COPCs, equilibrium may be dominated by adsorption processes. However, the concurrent release of other constituents (e.g., dissolved organic carbon, other ions) will also impact the results by modifying the solution characteristics of the aqueous phase. [For example, the dissolution of organic carbon from a waste has been shown to increase the solubility of copper in municipal solid waste incinerator (MSWI) bottom ash and several metals in matrices containing organic matter (van der Sloot, personal communication, 2002).] The two approaches that have been considered for achieving the objective of measuring solubility and

release as a function of pH are (a) static (controlled) pH testing at multiple pH values through use of a pH controller at desired set points (van der Sloot *et al.*, 1997), and (b) a series of parallel extractions of multiple sample aliquots using a range of additions of acid or alkali to achieve the desired range of end point pH values (Environment Canada and Alberta Environmental Center, 1986; Kosson *et al.*, 1996; Kosson and van der Sloot, 1997; prEN14429, 2001). Both testing approaches have been shown to provide similar results (van der Sloot and Hoede, 1997), including determination of both the acid/base titration buffering capacities of the tested material and the characteristic behavior of the constituents of potential concern. The static pH approach has the advantage of being able to achieve desired pH end points with a high degree of accuracy. The parallel extraction approach has the advantage of mechanical simplicity. The range of pH examined should include the extreme values of pH anticipated under field conditions and the pH when controlled by the tested material (i.e., "natural" or "own" pH). Thus, although the recommended method below provides a full characteristic behavior curve (i.e., for Tier 2, level B testing), an abbreviated version based on three analysis points may be used for simplified testing (i.e., for Tier 2A). The recommended method below is also analogous to CEN TC 292 Characterization of Waste–Leaching Behavior Test–pH Dependence Test with Initial Acid/Base Addition (prEN14429, 2001).

SR002.1 (alkalinity, solubility and release as a function of pH). This protocol consists of 11 parallel extractions of particle size reduced material at a liquid-to-solid ratio of 10 mL extractant/g dry sample. An acid or base addition schedule is formulated for 11 extracts with final solution pH values between 3 and 12, through addition of aliquots of HNO_3 or KOH as needed. The exact schedule is adjusted based on the nature of the material; however, the range of pH values includes the natural pH of the matrix that may extend the pH domain (e.g., for very alkaline or acidic materials). Using the schedule, the equivalents of acid or base are added to a combination of deionized (DI) water and the particle size reduced material. The final liquid–solid (LS) ratio is 10 mL extractant/g dry sample which includes DI water, the added acid or base, and the amount of moisture that is inherent to the waste matrix as determined by moisture content analysis. The 11 extractions are tumbled in an end-over-end fashion at 28 $\pm$ 2 rpm. Contact time is a function of the selected maximum particle size, with an extraction period of 48 h for the base case of 2 mm maximum particle size. Following gross separation of the solid and liquid phases by centrifugation or settling, leachate pH

Table 2. Comparison of recommended leaching protocols and applications.

Tier	Test name	Purpose	Methodology	Output	Application
1	AV001.1	To determine the potentially extractable content of constituents under environmental conditions.	Parallel extractions at pH 4 and 8 in DI water; Liquid-to-solid (LS) ratio of 100 mL/g; contact time dependent on particle size.	Availability at pH 4. Availability at pH 8.	Screening: conservative release estimate. Characterization: realistic source term for modeling mass transport-controlled release.
1	AV002.1	To determine the potentially extractable content of constituents under environmental conditions.	Single extraction using 50 mM EDTA; LS ratio of 100 mL/g; contact time dependent on particle size	Availability in EDTA.	Screening: conservative release estimate. Characterization: realistic source term for modeling mass transport-controlled release.
2	SR002.1	To obtain solubility and release data as a function of leachate pH	Multiple parallel extractions using DI water and HNO_3 or KOH; LS ratio of 10 mL/g; contact time dependent on particle size.	Material-specific acid/base titration curve. Solubility and release as a function of pH.	Characterization: detailed behavior of COPC as a function of pH. Compliance: abbreviated protocol to indicate consistency with previous characterization.
2	SR003.1	To estimate pore water conditions by obtaining solubility and release data as a function of LS ratio.	Multiple parallel extractions using DI water; LS ratios of 0.5 to 10 mL/g; contact time dependent on particle size.	Solubility and release as a function of LS ratio.	Characterization: detailed behavior of COPC as a function of LS ratio. Compliance: abbreviated protocol to indicate consistency with previous characterization.
3	MT001.1	To determine mass transfer parameters. To estimate rate of release under continuously saturated conditions.	Semidynamic tank leaching of monolithic material; Liquid-to-surface-area ratio of 10 [mL/cm^2]	Observed constituent diffusivity. Rate and cumulative release of constituent release under continuously saturated conditions.	Characterization: detailed leaching mechanisms and rate of release under mass-controlled leaching scenario. Compliance: abbreviated to indicate consistency with previous characterization.
3	MT002.1	To determine mass transfer parameters. To estimate rate of release under continuously saturated conditions.	Semidynamic tank leaching of compacted granular material; Liquid-to-surface-area ratio of 10 [mL/cm^2]	Observed constituent diffusivity. Rate and cumulative release of constituent release under continuously saturated conditions.	Characterization: detailed leaching mechanisms and rate of release under mass-controlled leaching scenario. Compliance: abbreviated to indicate consistency with previous characterization.

measurements are taken, and the phases are separated by vacuum filtration through 0.45-μm polypropylene filtration membranes. Analytical samples of the leachates are collected and preserved as appropriate for chemical analysis. The acid and base neutralization behavior of the materials is evaluated by plotting the pH of each extract as a function of equivalents of acid or base added per gram of dry solid. Equivalents of base are presented as opposite sign of acid equivalents. Concentration of constituents of interest for each extract is plotted as a function of extract final pH to provide liquid-solid partitioning equilibrium as a function of pH. Figure 2 (a) and (b) shows conceptual output from the recommended SR002.1 protocol with the recognition that a broad range of behaviors is possible. In Fig. 3(a), the output data of the SR002.1 protocol for a cementitious synthetic waste matrix (Garrabrants, 2001) is compared to the total elemental content and constituent availability (Tier 1 value).

The abbreviated version of the SR002.1-A (Alkalinity, Solubility, and Release as a Function of pH) protocol consists of three parallel extractions of particle size reduced

material at a liquid-to-solid ratio of 10 mL extractant/g dry sample. The selection of the target pH values is dependent on the natural pH of the material. If the natural pH is <5, then natural pH, 7 and 9, are selected as the target pH values. If the natural pH ranges between 5 and 9, then 5, 7, and 9 are selected as the target pH values, and if the natural pH is >9, then 5, 7, and natural pH are selected as the target pH values.

Tier 2—solubility and release as a function of LS ratio

The objective of this test is to determine the effect of low liquid-to-solid ratio on liquid–solid partitioning equilibrium when the solution phase is controlled by the tested material. This is used to approximate initial pore-water conditions and initial leachate compositions in many percolation scenarios (e.g., monofills). This objective is accomplished by a series of parallel extractions using multiple aliquots of the tested material at different LS ratio with deionized water to achieve the desired range
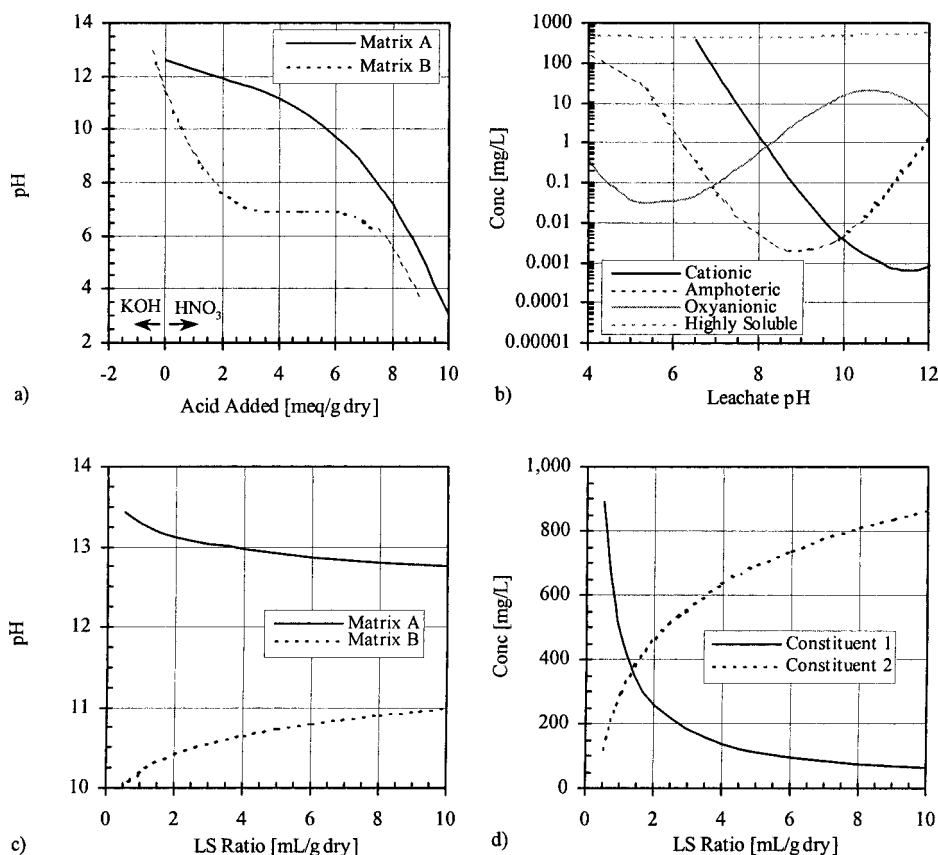

Figure 2.   Conceptual data obtained using equilibrium-based testing protocols: (**a**) titration curve (SR002.1), (**b**) constituent release as a function of pH (SR002.1), (**c**) pH as a function of LS ratio (SR003.1), and (**d**) constituent concentration as a function of LS ratio (SR003.1).
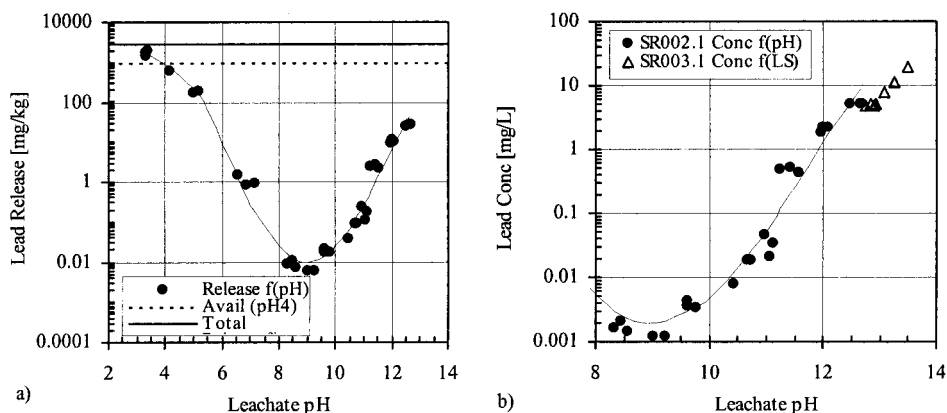
Figure 3. Actual data obtained using equilibrium-based testing protocols from a cementitious synthetic waste: (**a**) lead release as a function of pH compared to lead availability and total lead content, and (**b**) comparison of SR002.1 and SR003.1 concentration data.

of conditions. When necessary, results can be extrapolated to lower LS ratio than readily achieved under typical laboratory conditions. The range of LS ratio examined should include the condition used for solubility and release as a function of pH testing (i.e., LS = 10 mL/g) and the lowest LS practically achievable that approaches typical pore water solutions (i.e., LS = 0.5 mL/g). Thus, although the recommended method below provides a full characteristic behavior curve (i.e., for Tier 2, level B testing), an abbreviated version based on two analysis points may be used for simplified testing (i.e., for Tier 2A). [The abbreviated methods for testing solubility as a function of pH (three points) and solubility as a function of LS (two points) include one common point in both tests. Thus, for integrated testing under Tier 2, four analysis points are recommended.]

For some materials, LS <2 mL/g may be difficult to achieve with sufficient quantity of eluate for analysis due to limitations of solid–liquid separation. In addition, the formation of leachate colloids can result in overestimation of release for some metals and organic contaminants. Use of a column test is an alternative to use of batch testing for measuring release as function of LS. A column test (prEN14405, 2001), similar to the Dutch standard column test (NEN 7343, 1995), has been developed within the European Standardization Organization CEN.

SR003.1 (solubility and release as a function of LS ratio). This protocol consists of five parallel batch extractions over a range of LS ratios (i.e., 10, 5, 2, 1, and 0.5 mL/g dry material), using DI water as the extractant with aliquots of material that has been particle size reduced. The mass of material used for the test varies with the particle size of the material. All extractions are conducted

at room temperature (20 ± 2°C) in leak-proof vessels that are tumbled in an end-over-end fashion at 28 ± 2 rpm. Contact time is a function of the selected maximum particle size, with an extraction period of 48 h for the base case of 2 mm maximum particle size. Following gross separation of the solid and liquid phases by centrifugation or settling, leachate pH and conductivity measurements are taken, and the phases are separated by a combination of pressure and vacuum filtration using 0.45-μm polypropylene filter membrane. The five leachates are collected, and preserved as appropriate for chemical analysis. Figure 2 (c) and (d) shows conceptual output from the recommended SR003.1 protocol with the recognition that a broad range of behaviors is possible. In Fig. 3(b), the output data of equilibrium-based protocols (SR002.1 and SR003.1) are compared for a cementitious synthetic waste matrix (Garrabrants, 2001).

The abbreviated version, SR003.1-A (Solubility and Release as a Function of LS Ratio) protocol consists of two parallel extractions of particle size reduced material using DI water at liquid-to-solid ratio of 10 and 0.5 mL extractant /g dry sample, respectively. The extraction at an LS ratio of 10 mL/g may be the same sample as used in SR002.1-A to reduce the required number of analyses.

Tier 3—mass transfer rate (monolithic and compacted granular materials)

The objective of mass transfer rate tests is to measure the rate of COPC release from a monolithic material (e.g., solidified waste form or concrete matrix) or a compacted granular material. Results of these tests are to estimate intrinsic mass transfer parameters (e.g., observed diffusivities for COPCs) that are then used in conjunction with other testing results and assessment models to estimate

release. Results of these tests reflect both physical and chemical interactions within the tested matrix, thus requiring additional test results for integrated assessment. Although the recommended methods are derivatives of ANS 16.1 (ANS, 1986), a leachability index is not assumed nor used as a decision criterion. The recommended methods below are also analogous to NEN 7345 (NEN 7345, 1994) and methods under development by CEN TC 292.

MT001.1 (mass transfer rates in monolithic materials). This protocol consists of tank leaching of continuously water-saturated monolithic material with periodic renewal of the leaching solution. The vessel and sample dimensions are chosen so that the sample is fully immersed in the leaching solution. Cylinders of 2-cm minimum diameter and 4-cm minimum height or 4-cm minimum cubes are contacted with DI water using a liquid-to-surface area ratio of 10 mL of DI water for every cm^2 of exposed solid surface area. Larger cylinder sizes are recommended for treated materials that have a particle size greater than 2 mm prior to solidification. Typically, the cylinder diameter and height or cube dimension should be at least 10 times the maximum particle size of the material contained therein. Leaching solution is exchanged with fresh DI water at predetermined cumulative times of 2, 5, and 8 h, 1, 2, 4, and 8 days. [This schedule may be extended for additional extractions to provide more information about longer term release. The recommended schedule extension would be additional cumulative times of 14 days, 21 days, 28 days, and every 4 weeks thereafter as desired. Alternately, the duration of the test may be shortened (e.g., cumulative time of 4 days) for compliance testing.] This schedule results in seven leachates with leaching intervals of 2, 3, 3 and 16 h, 1, 2, and 4 days. At the completion of each contact period, the mass of the monolithic sample after being freely drained is recorded to monitor the amount of leachant absorbed into the solid matrix. The solution pH and conductivity for each leachate is measured for each time interval. A leachate sample is prepared for chemical analysis by vacuum filtration through a 0.45-μm pore size polypropylene filtration membrane and preservation as appropriate. Leachate concentrations are plotted as a function of time along with the analytical detection limit and the equilibrium concentration determined from SR002.1 at the extract pH for quality control to ensure that release was not limited by saturation of the leachate. Cumulative release and flux as a function of time for each constituent of interest are plotted and used to estimate mass transfer parameters (i.e., observed diffusivity). Figure 4 shows sample output data from the MT001.1 test for a solidified waste matrix (van der Sloot, 1999). The solubility data

shown in the figure corresponds to data derived from SR002.1.

MT002.1 (mass transfer rates in compacted granular materials). This protocol consists of tank leaching of continuously water-saturated compacted granular material with intermittent renewal of the leaching solution. This test is used when a granular material is expected to behave as a monolith because of compaction during field placement. An unconsolidated or granular material is compacted into molds at optimum moisture content using a modified Proctor compactive effort (NEN 7347, 1997). A 10-cm diameter cylindrical mold is used and the sample is packed to a depth of 7 cm. The mold and sample are immersed in deionized water such that only the surface area of the top face of the sample contact the leaching medium, without mixing. The leachant is refreshed with an equal volume of deionized water using a liquid to surface area ratio of 10 mL/cm^2 (i.e., LS ratio of 10 cm) at cumulative times of 2, 5, and 8 h, 1, 2, 4, and 8 days. This schedule results in seven leachates with leaching intervals of 2, 3, 3, and 16 h, 1, 2, and 4 days. The solution pH and conductivity for each leachate is measured for each time interval. A leachate sample is prepared for chemical analysis by vacuum filtration through a 0.45-μm pore size polypropylene filtration membrane and preservation as appropriate. Leachate concentrations are plotted as a function of time along with the analytical detection limit and the equilibrium concentration determined from SR002.1 at the extract pH for quality control. Cumulative release and flux as a function of time for each constituent of interest are plotted and used to estimate mass transfer parameters (i.e., observed diffusivity).

RELEASE ASSESSMENT ESTIMATES

Release estimates may be obtained for site-specific and management scenario-specific cases when appropriate environmental data (e.g., precipitation frequency and amounts) and design information (e.g., placement geometry, infiltration rates) are available. For many situations, site-specific information either may not be readily available or may not be necessary (e.g., as in the case when the intent of testing is only to provide uniform side-by-side comparisons of treatment processes). For these situations, default scenarios may be defined; an application of this approach is provided in the companion paper (Sanchez *et al.*, 2002c). These default scenarios are for illustrative purposes only, and other parameter values may be more appropriate for different management scenarios and geographic locations.
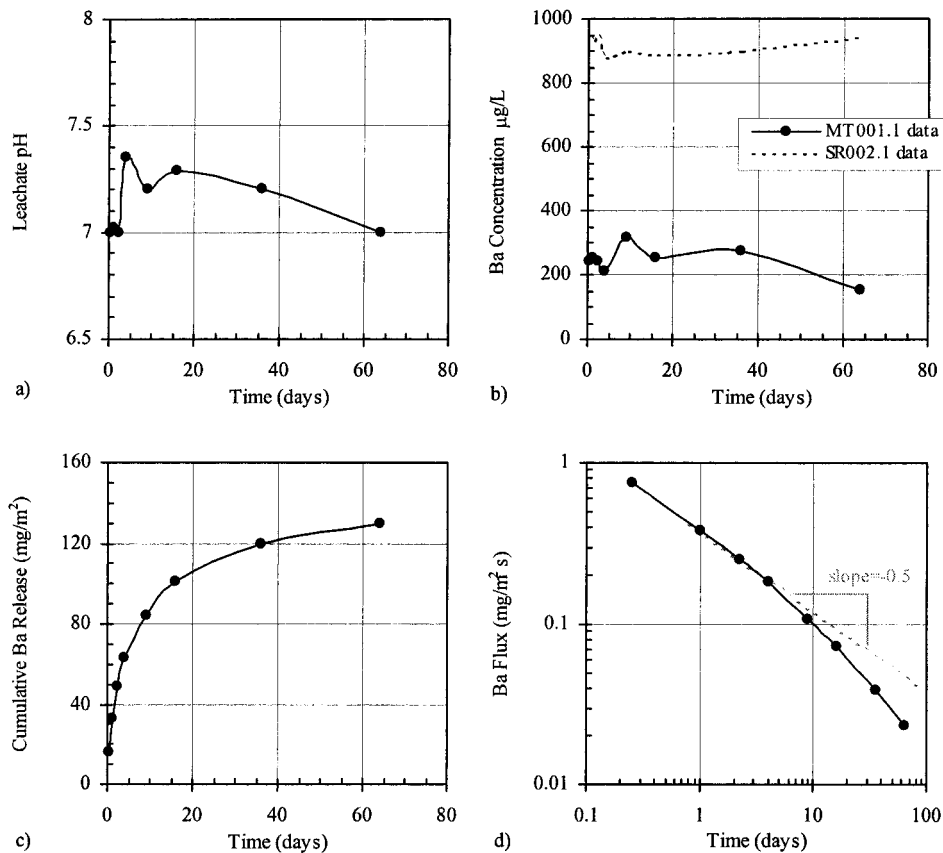
Figure 4. Actual data obtained using MT001.1 protocol from a stabilized waste (van der Sloot, 1999): (**a**) leachate pH as a function of cumulative time, (**b**) comparison of leachate barium concentration (MT001.1) and barium solubility as a function of pH (SR002.1), (**c**) cumulative release of barium as a function of cumulative time, and (**d**) barium flux as a function of mean cumulative time.

Percolation-controlled scenario

Percolation-controlled release occurs when water flows through a permeable fill with low infiltration rate and low liquid-to-solid ratio (Fig. 5). In this case, local equilibrium at field pH is assumed to be limiting release. The information required to estimate constituent release during this scenario is the (a) field geometry, (b) field density, (c) anticipated infiltration rate, (d) anticipated field pH, (e) anticipated site-specific liquid-to-solid ratio, and (f) constituent solubility at the anticipated field pH. The anticipated site-specific liquid-to-solid (LS_{site}) ratio represents the cumulative liquid-to-solid ratio that can be expected to contact the fill over the estimated time period. It is based on the infiltration rate, the contact time, the fill density, and the fill geometry, and can be determined according to (Hjelmar, 1990; Kosson *et al.*, 1996):

$$LS_{site} = 10 \frac{inf \cdot t_{year}}{\rho \cdot H_{fill}} \qquad (2)$$

where, LS_{site} is the anticipated site-specific liquid-to-solid

ratio (L/kg); *inf* is the anticipated infiltration rate (cm/year); t_{year} is the estimated time period (year); ρ is the fill density (kg/m³); H_{fill} is the fill depth (m); and 10 is a conversion factor (10 L/cm-m²).

Over an interval of 100 years or longer, LS_{site} values greater than 10 mL/g may be obtained for cases that have relatively high rates of infiltration or limited placement depth (Kosson *et al.*, 1996; Schreurs *et al.*, 2000). However, for many disposal scenarios, the observed LS_{site} has been less than 2 L/kg over a period of ca. 10 years, and for an isolated landfill site with reduced infiltration, it may take 1,000 years to reach LS_{site} of 1 L/kg (Johnson *et al.*, 1998, 1999; Hjelmar *et al.*, 2001).

An estimate of the cumulative mass release per unit mass of material can then be obtained using the anticipated site-specific LS ratio and the constituent solubility at the anticipated field pH ($S_{field\ pH}$) according to:

$$M_{mass}^{t_{year}} = (LS_{site})(S_{field\ pH}) \qquad (3)$$

where, $M_{mass}^{t_{year}}$ is the cumulative mass of the constituent

Scenario characteristics
- Granular or highly permeable material
- Low infiltration rate
- Low liquid-solid ratios [mL/g]

Site information
- Infiltration rate   *inf*
- Fill density ρ
- Fill geometry H_{fill}
- Field pH

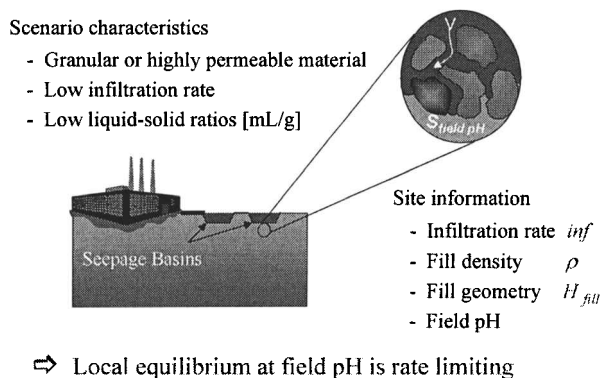⇨ Local equilibrium at field pH is rate limiting

Figure 5.   Release scenario: percolation.

released (mass basis) at time t_{year} (mg/kg); and $S_{\text{field pH}}$ is the constituent solubility (mg/L) at the pH value corresponding to field pH.

Mass transfer-controlled scenario

Mass transfer-controlled scenario occurs when infiltrating water is diverted around a low permeability fill or prevented from percolating through the fill due to an impermeable overlay (Fig. 6) or adjacent high permeability channels. In this case, mass transport within the solid matrix is rate limiting. The information required to estimate constituent release during such scenario are the (a) field geometry, (b) field density, (c) initial leachable content, and (d) observed diffusivity of the species of concern.

The mechanisms of release under mass transfer control can be quite complex and constituent specific. The rate of COPC diffusion through the material can be retarded by surface reactions or precipitation of insoluble compounds. Alternately, mass transport may be enhanced by species complexation or mineral phase dissolution. Numerical techniques often are required to fully describe release under complex mechanistic conditions. Sophisticated models have been developed, or are under development, to account for dissolution/precipitation phenomena (Batchelor, 1990, 1992, 1998; Cheng and Bishop, 1990; Hinsenveld, 1992; Batchelor and Wu, 1993; Hinsenveld and Bishop, 1996; Moszkowicz *et al.*, 1996, 1997, 1998; Sanchez, 1996; Baker and Bishop, 1997), sorption/desorption phenomena, and material heterogeneity (Sanchez *et al.*, 2002b).

Fickian diffusion model. The Fickian diffusion model, based on Fick's second law, assumes that the species of interest is initially present throughout the homogeneous porous medium at uniform concentration and considers that mass transfer takes place in response to concentration gradients in the pore water solution of the porous medium. The assumptions and release estimation approach shown here is most appropriate for release scenarios for which only highly soluble species are a concern or for which external stresses (e.g., pH gradients, carbonation, redox changes) are not significant.

In the classical representation of the diffusion model, two coupled parameters characterize the magnitude and rate of the release: C_0, the initial leachable content (e.g., available release potential, total elemental content) and D_{obs}, the observed diffusivity of the species in the porous medium. (The value used for the initial leachable content and the determined observed diffusivity are coupled parameters such that the same set of parameters obtained from experimental data must be used in determining long-term release estimates.) When the species of concern is not depleted over the time period of interest, the cumulative mass release can be described by a one-dimensional semi-infinite geometry. Depletion is considered to occur when more than 20% of the total leachable content has been released (de Groot, 1993).

For a one-dimensional geometry, an analytical solution for Fickian diffusion is provided by Crank (1975), with the simplifying assumption of zero concentration at the solid–liquid interface (i.e., case of a sufficient water renewal; infinite bath assumption):

$$M^t_{\text{area}} = 2 \cdot \rho \cdot C_0 \left(\frac{D^{\text{obs}} \cdot t}{\pi} \right)^{1/2} \tag{4}$$

where M^t_{area} is the cumulative mass of the constituent released (surface area basis) at time t (mg/m^2)]; C_0 is the initial leachable content (i.e., available or total elemental content) (mg/kg); ρ is the sample density (kg/m^3); t is the time interval (s); and, D^{obs} is the observed diffusivity of the species of concern (m^2/s).

Scenario characteristics
- Low permeability material
- High infiltration rate
- High liquid-surface area ratios

Site information
- Fill density
- Fill geometry   *S, V*
- Fill porosity

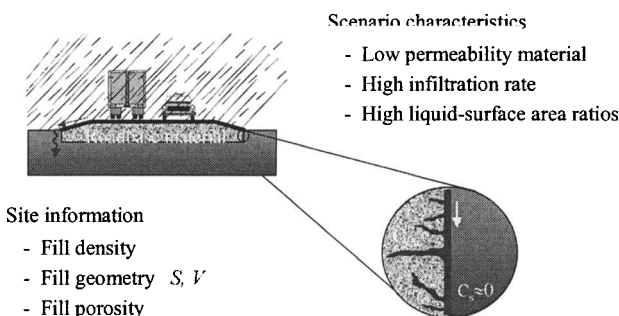⇨ Mass transport within solid matrix is rate limiting

Figure 6.   Release scenario: diffusion-controlled scenario.

The test conditions for the MT series protocols (i.e., MT001.1 and MT002.1) are designed to ensure a non-depleting matrix and approximate the zero-concentration boundary, although field conditions may not satisfy these simplifications for many cases, and the resulting release estimate may overestimate release. Therefore, other modeling approaches may be required to more accurately extrapolate to field conditions.

In release scenarios for which COPC depletion does not occur and Fickian diffusion is considered the dominant release mechanism, the mass release is proportional to release time by a $t^{1/2}$ relationship. After a log transform, Equation (4) becomes:

$$\log M_{\text{area}}^t = \log \left[2 \cdot \rho \cdot C_0 \left(\frac{D^{\text{obs}}}{\pi} \right)^{1/2} \right] + \frac{1}{2} \log t \quad (5)$$

Thus, the logarithm of the cumulative release plotted vs. the logarithm of time is expected to be a straight line with a slope of 0.5. Often, initial release as observed from laboratory testing reflects wash off or dissolution of surface-associated constituents. The apparent constituent release then may be followed by diffusion-controlled release. Mass release over this initial time when surface phenomena are observed would result in a line with a slope greater than 0.5. In these cases, only the data points reflecting diffusion-controlled release are used to estimate observed diffusivity. The initial release should be verified to be insignificant in relation to the long-term field estimate of release (see Sanchez *et al*, 2002c, for an illustration of this phenomena).

Estimation of observed diffusivity. Under the assumptions of the Fickian diffusion model, an observed diffusivity can be determined for each leaching interval where the slope is 0.5 ± 0.15 by (de Groot and van der Sloot, 1992):

$$D_i^{\text{obs}} = \pi \left(\frac{M_{\text{area}}^{t_i}}{2 \cdot \rho \cdot C_0 (\sqrt{t_i} - \sqrt{t_{i-1}})} \right)^2 \quad (6)$$

where D_i^{obs} is the observed diffusivity of the species of concern for leaching interval i (m²/s); $M_{\text{area}}^{t_i}$ is the mass released (surface area basis) during leaching interval i (mg/m²); t_i is the contact time after leaching interval i (s); and, t_{i-1} is the contact time after leaching interval $i - 1$ (s).

The overall observed diffusivity is then determined by taking the average of the interval observed diffusivities.

Release estimates. An estimate of the cumulative mass release for the management scenario can then be obtained using the analytical solution [Equation (4)] over the anticipated assessment interval. When COPC release per unit mass of material is desired, conversion based on material field geometry can be applied to Equation (4).

$$M_{\text{mass}}^t = 2 \cdot C_0 \cdot \frac{S}{V} \cdot \left(\frac{D^{\text{obs}} \cdot t}{\pi} \right)^{1/2} \quad (7)$$

where, M_{mass}^t is the cumulative mass of the constituent released (mass basis) at time t (mg/kg); S is the fill surface area (m²); and V is the fill volume (m³).

In the case where initial surface wash-off is considered to provide significant contribution to the release prediction (i.e., >5% of cumulative release), release from initial surface wash-off is added to release estimate from diffusion-controlled phenomena. An estimate of the cumulative mass release can then be obtained using:

$$M_{\text{mass}}^t = M_{\text{area}}^{\text{wash-off}} \cdot S + 2 \cdot C_0 \cdot \frac{S}{V} \cdot \left(\frac{D^{\text{obs}} \cdot t}{\pi} \right)^{1/2} \quad (8)$$

where, $M_{\text{area}}^{\text{wash-off}}$ is the mass of constituent released (surface area basis) from surface wash-off (mg/m²).

When depletion of the COPC is anticipated to occur over the release interval, three-dimensional analysis using finite body models may be required to estimate cumulative release. Analytical solutions may be found for different geometries in mass transport literature (Crank, 1975) or simplifying assumptions may be applied to validate the above 1D approach (Kosson *et al*., 1996). Alternately, numerical methods may be used to solve the Fickian diffusion equation in three dimensions (Barna, 1994).

The above estimates represent a conservative approach for most mass transfer-controlled release scenarios where significant external stresses are not present. A zero surface concentration assumes a maximum gradient, or driving force, for mass transport (infinite bath assumption). In the case of slow water flow past the surface or small liquid-to-surface area ratios, accumulation of the COPC concentration in the leachate reduces the concentration gradient and limits leachate concentration to the mass of COPC in equilibrium with the solid phase. Thus, the upper bound (or maximum concentration) for mass transfer-controlled release should be estimated using release estimates obtained from equilibrium assumptions (e.g., Tier 2 testing in conjunction with percolation controlled release).

Other modeling considerations

Mass transport modeling approaches (Garrabrants, 2001; Garrabrants *et al*., 2002; Sanchez *et al*., 2001; Tiruta-Barna *et al*., 2002) are under development to address environmental conditions that are more likely to be encountered in the field such as intermittent wetting under

varied environmental conditions (i.e., relative humidity and CO_2 content). Additional modeling also has been done to relate column test results to field leaching through application of geochemical speciation (Dijkstra *et al.*, 2002). These models can provide more accurate release estimates, but typically require additional information (experimental and field) and greater expertise for use. The simple modeling approach provided here is intended to be a conservative, first-order approximation that will result in overestimation of actual release for most cases.

EXAMPLE APPLICATIONS OF THE FRAMEWORK

Important potential applications of the leaching framework defined here include (a) the comparative assessment of waste treatment processes, such as for determinations of equivalent treatment under RCRA; (b) estimating environmental impacts from utilization of secondary materials in construction applications; or (c) estimating releases from large scale waste monofills. For these cases, Tier 2B and Tier 3B testing is recommended for initial evaluation. An example of this application is provided in the accompanying paper (Sanchez *et al.*, 2002c). Subsequently, Tier 2A testing can be used to establish consistency between the materials initially tested and other similar materials.

ECONOMIC CONSIDERATIONS

The more extensive testing recommended in the proposed framework will obviously increase initial testing costs. However, these initial costs should be offset by several factors. First, detailed characterization of a material is only necessary initially to define its characteristic leaching properties, and only for materials that are produced in relatively large quantities. Subsequently, much less testing is needed to verify that new samples conform to the previously established properties. Second, cost savings should be realized through the framework by enabling alternative management strategies that are not possible under the current rigid system. Treatment processes evaluated under this system will be better targeted to reducing leaching under field scenarios. Reduced treatment costs may be achieved in many cases (however, treatment costs may increase in cases where treatment processes were only effective at meeting TCLP, but were ineffective at reducing leaching in the field to levels consistent with risk-based end points). In addition, the potential for environmental damage and future liability will be reduced because of the closer relationship be-

tween testing and field performance. Costs for Tier 1 and Tier 2A testing should be of the same order of magnitude as current TCLP testing. Reductions in costs are anticipated as the methods become commercialized and data interpretation is automated.

CONCLUSIONS

The proposed framework presents an approach to evaluate the leaching potential of wastes over a range of values for parameters that have a significant impact on constituent leaching (e.g., pH, LS, and waste form) and considering the management scenario. This approach presents the potential to estimate leaching much more accurately (than many currently used leach tests), relative to field leaching, when conditions for leach test data are matched with field conditions. The greater accuracy of the proposed approach makes it a useful tool for examining waste and assessing the environmental soundness of a range of waste management options as well as for assessing the effectiveness of proposed waste treatment methods. In addition, the proposed framework provides flexibility to the end user to select the extent of testing based on the level of information needed, and readily permits the incorporation of new testing methods and release models as they are developed for specific applications. Appropriately used in waste regulatory programs, this approach could make those programs substantially more cost-effective and protective of the environment. The flexibility of the proposed approach allows for development of the framework to provide a greater degree of tailoring to site conditions, to account for the effects of other waste leaching parameters critical to a particular site. Reliance on a tiered approach to testing can also make this approach more economical for smaller waste volumes and therefore more broadly feasible.

Kosson during the development of the test methods. The authors also gratefully acknowledge the thoughtful comments and feedback of the anonymous reviewers and the assistance of the Editor, Dr. D. Grasso, lead author of the USEPA Science Advisory Board Review (1999) for which this paper is primarily in response. The view points expressed in this paper are solely the responsibility of the authors and do not necessarily reflect the view or endorsement of the USEPA.

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APPENDIX

A.1. AV002.1 (AVAILABILITY AT PH 7.5 WITH EDTA)

1. Scope

1.1. This test method measures the maximum quantity, or mobile fraction of the total content, of inorganic constituents in a solid matrix that potentially can be released into solution. An extraction fluid of 50 mM ethylenediamine-tetraacetic acid (EDTA) is used to chelate metals of interest in solution at near neutral pH during a single extraction.

1.2. This is a candidate screening protocol (Tier 1).

1.3. This test method is not intended for the release characterization of organic constituents.

2. Cited Protocols

2.1. ASTM (1980) "Standard Method for Water (Moisture) Content of Soil, Rock, and Soil–Aggregate Mixtures D 2261-80," Philadelphia, PA: American Society for Testing and Materials.

2.2. pH001.0 (pH Titration Pretest).

2.3. AW001.0 (Acid Washing of Laboratory Equipment).

2.4. PS001.1 (Particle Size Reduction).

3. Summary of the Test Method

Constituent availability is determined by a single challenge of an aliquot of the solid matrix to dilute acid or base in deionized (DI) water with a chelating agent (Garrabrants and Kosson, 2000). A solution of 50 mM ethylenediamine-tetraacetic acid (EDTA) in DI water is used to minimize liquid phase solubility limitations for cationic constituents with very low solubility (i.e., Pb, Cu, Cd). For most materials, this test is conducted on material that has been particle size <2 mm and a minimum sample mass of 8 g dry sample is used. (The particle size, sample mass, and contact time shown here represent a typical base case scenario. Alternate sample masses and contact times are required for materials where particle size reduction to <2 mm is either impractical or unnecessary (see accompanying text). In all extractions, a liquid-to-solid (LS) ratio of 100 mL extractant/g dry sample and a contact time of 48 h are used to reduce mass transfer rate limitations. Extracts are tumbled in an end-over-end fashion at 28 ± 2 rpm at room temperature ($20 \pm 2°C$). After the appropriate contact time, the leachate pH value of the extraction is measured. The retained extract is filtered through $0.45\text{-}\mu m$ pore size polypropylene filtration membranes, and the analytical sample is saved for subsequent chemical analysis.

The required end point pH value for the optimized extraction of cations and anions is 7.5 ± 0.5. The final specified pH value is obtained by addition of a predetermined equivalent of acid or base prior to the beginning of the extraction. The amount of acid or base required to obtain the final end point pH value is specified by a titration pretest of the material that follows the "pH001.0 (pH Titration Pretest)" protocol with the modifications that the titration solution is 50-mM EDTA solution rather than DI water. The required pH range for this pretest is limited to pH values 5 through 8. Because "AV002.1 (availability at pH 7.5 with EDTA)" is a batch extraction procedure used for materials that may be heterogeneous in acid neutralization capacity, extractions at the limiting values of 7.0 and 8.0 are recommended in addition to the pH target value extraction. The leachate with a pH value closest to 7.5 is saved for chemical analysis while the others are discarded.

4. Significance and Use

The results from this test are used to determine the maximum quantity, or the fraction of the total constituent content, of inorganic constituents in a solid matrix that potentially can be released from the solid material in the presence of a strong chelating agent such as EDTA. The chelated availability, or mobile fraction, can be considered (1) the thermodynamic driving force for mass transport through the solid material or (2) the potential long-term constituent release. Also, a mass balance based on the total constituent concentration provides the fraction of a constituent that may be chemically bound, or immobile in geologically stable mineral phases. The availability represents a potential for constituent release, not an actual release measurement. This procedure measures availability in relation to the release of anions at an end point pH of 7.5 ± 0.5 and cations under enhanced liquid-phase solubility due to complexation with the chelating agent.

5. Apparatus

5.1. *Extraction Vessel*—a wide-mouth container, constructed of high-density polyethylene that does not preclude headspace (e.g., Nalgene #3120-9500 or equivalent). The vessel must have a leak-proof seal that can sustain the required end-over-end tumbling. The container must be of sufficient volume to accommodate both a minimum solid sample and a leachant volume based on a LS ratio of 100 mL extractant/g dry sample. If centrifugation is to be used for gross phase separation, the extraction vessel should be capable of withstanding centrifugation at 4000 rpm for a minimum of 10 min.

5.2. *Extraction Apparatus*—rotary tumbler capable of rotating the extraction vessels in an end-over-end fashion at constant speed of 28 ± 2 rpm (e.g., Analytical Testing, Werrington, PA, or equivalent).

5.3. *Filtration Apparatus*—pressure or vacuum filtering apparatus (e.g., Nalgene #300-4000, or equivalent).

5.4. *Filtration Membranes*—0.45-μm pore size polypropylene filtration membrane (e.g., Gelman Sciences GH Polypro #66548, Fisher Scientific, or equivalent).

5.5. *pH Meter*—standard, two point calibration pH meter (e.g., Accumet 20, Fisher Scientific, or equivalent).

5.6. *Adjustable Pipetter*—Oxford Benchmate series or equivalent with disposable tips (delivery range will depend on material neutralization capacity and acid strength).

5.7. *Centrifuge (optional)*—e.g., RC5C, Sorvall Instruments, Wilmington, DE, or equivalent.

6. Reagents and Materials

6.1. *Reagent-Grade Water*—deionized (DI) water must be used as the major extractant in this procedure. DI water with a resistivity of 18.2 MΩ can be provided by commercially available water deionization systems (e.g., Milli-Q Plus, Millipore Corp., Bedford, MA, or equivalent).

6.2. *50 mM EDTA Solution*—prepared by dissolving 18.61 g of disodium ethylenediamine-tetraacetate dihydrate—$C_{10}H_{14}N_2O_8Na_2 \cdot 2H_2O$ (Sigma Chemical, St. Louis, MO, or equivalent) in 1 L of DI water.

6.3. *2 N Nitric Acid Solution*—prepared by diluting Tracemetal Grade Nitric Acid (Fisher Scientific or equivalent) with deionized water.

6.4. *1 N Potassium Hydroxide Solution*—reagent Grade (Fisher Scientific or equivalent).

7. Acid Washing Procedure

Because the concentrations of inorganic constituents in leachates may be very low (i.e., <10 μg/L), all laboratory equipment that comes in contact with the material, the extraction fluid, or the leachant must be rinsed with 10% nitric acid followed by three rinses with DI water to remove residual inorganic deposits following "AW001.0 (Acid Washing of Laboratory Equipment)."

8. Initial Sample Preparation

8.1. *Particle Size Reduction*—depending on the nature of the material, a sufficient mass of the material should be particle size reduced to <2 mm using "PS001.1 (Particle Size Reduction)" protocol.

8.2. *Solids Content Determination*—it is necessary to know the solids content of the material being tested so that appropriate adjustments can be made to conduct the test under the specified LS ratio. Prior to the initiation of the test, a moisture content determination of the "as-received" material must be conducted using ASTM Method D 2261-80, "Standard Method for Laboratory Determination of Water (Moisture) Content of Soil, Rock, and Soil–Aggregate Mixtures." The solids content is calculated as the mass of the dried sample divided by the mass of "as received" material as in the following equation:

$$ SC = \frac{M_{dry}}{M_{rec}} \tag{A1-1} $$

where *SC* is the solids content (g dry/g); M_{dry} is the dry sample mass (g dry), and M_{rec} is the mass of the "as received" material (g).

9. AV002.1 Procedure

The AV002.1 protocol may be conducted only after the required equivalents of acid or base to reach the three specified extraction pH values are determined. The three extraction pH values should include the pH target value

Table A1-1. Example schedule of acid addition and 50-mM EDTA makeup for a dry equivalent sample mass of 8 g dry and a dry basis moisture content of 0.1 mL/g dry for the "AV002.1 (Availability at pH 7.5 with EDTA)" protocol.

Extract no.	End point solution pH	Equivalents of acid to add (mEq/g dry)	Volume of 2 N HNO₃ (mL)	Volume of moisture in sample (mL)	Volume of 50 mM EDTA makeup (mL)
1—limit	7.0	1.05	4.20	0.8	795.00
2—target	7.5	0.93	3.48	0.8	795.72
3—limit	8.0	0.63	2.52	0.8	796.68

(i.e., 7.5) plus the two-pH limiting values (i.e., 7.0 and 8.0). Additionally, the volume of 50-mM EDTA solution required to obtain a total LS ratio of 100 mL/g dry material should be calculated. Table A1-1 shows an example schedule of HNO_3 additions following the pH001.0 protocol for a dry equivalent sample mass of 8 g (<2 mm particle size) and a dry-basis moisture content of 10% (i.e., 0.1 mL/g dry)

9.1. Place the minimum dry equivalent sample mass (i.e., 8 g dry) into each of three high-density polyethylene bottles. Label each bottle with one of the above target pH values. The required equivalent mass of "as-received" material can be calculated following Equation (A1-4) if the solids content is known.

$$M_{rec} = \frac{M_{dry}}{SC} \tag{A1-4}$$

where M_{rec} is the the mass of the "as received" material (g), M_{dry} is the dry equivalent sample mass (i.e., 8 g dry for particle size <2 mm (g dry), and SC is the solids content of the material (g dry/g).

9.2. Add the appropriate makeup volume of 50-mM EDTA solution to each bottle as specified in a schedule of acid and base additions (e.g., Table A1-1).

9.3. Add the appropriate volume of 2 N HNO_3 or 1 N KOH required to achieve the end point pH values to each bottle with an automatic pipetter. Volumes of acid or base are specified by the predetermined schedule (e.g., Table A1-1).

9.4. Tighten the leak-proof lid for each bottle and tumble the three extracts in an end-over-end fashion at a speed of 28 ± 2 rpm at room temperature ($20 \pm 2°C$).

9.5. At the end of the equilibration period, remove the extraction vessels from the rotary tumbler.

9.6. Clarify the leachates by allowing the bottles to stand for 15 min. Alternately, centrifuge the bottles at 4000 ± 100 rpm for 10 ± 2 minutes.

9.7. Decant a minimum volume of clear, unpreserved supernatant from each bottle into suitable vessel to measure final solution pH.

9.8. Save the leachate with a pH value that is both within the target pH range (i.e., 7.5 ± 0.5) and closest to the target pH value (i.e., 7.5). The other extracts are discarded.

9.9. Separate the solid and liquid phases of the saved extract by vacuum filtration through a 0.45-μm pore size polypropylene filtration membrane. The filtration apparatus may be exchanged for a clean apparatus as often as necessary until all liquid has been filtered.

9.10. Collect, preserve, and store the amount of leachate required for chemical analysis.

10. AV002.1 Interpretation

After chemical analysis, the chelated availability can be determined for each "constituent of potential concern" (COPC). This availability can be calculated on a dry sample mass basis by multiplying the constituent concentration in the leachate by the test-specific LS ratio as shown in Equation (A1-5).

$$AVL_{EDTA} = C_{EDTA} \, LS \tag{A1-5}$$

where AVL_{EDTA} is the constituent availability using 50-mM EDTA (mg/kg dry), C_{EDTA} is the constituent concentration using 50 mM EDTA (mg/L), and LS is the test liquid to solid ratio (i.e., 100) (L/kg).

11. References

GARRABRANTS, A.C., and KOSSON, D.S. (2000). Use of a chelating agent to determine the metal availability for leaching from soils and wastes. *Waste Manage. Res*. **20**(2–3), 155–165.

A.2. SR002.1 (ALKALINITY, SOLUBILITY AND RELEASE AS A FUNCTION OF PH)

1. Scope

1.1. This test method provides the acid/base titration buffering capacity of the tested material and the liquid–solid partitioning equilibrium of the "constituents of potential concern" (COPC) as a function of pH at a liquid-to-solid (LS) ratio of 10-mL extractant/g dry sample.

1.2. This is a characterization protocol (Tier 2b) designed to obtain detailed leachability information.

1.3. This test method is not intended for the determination of the solubility profile of organic constituents.

2. Cited Protocols

2.1. ASTM (1980) "Standard Method for Water (Moisture) Content of Soil, Rock, and Soil–Aggregate Mixtures D 2261-80," Philadelphia, PA: American Society for Testing and Materials.

2.2. pH001.0 (pH Titration Pretest).

2.3. AW001.0 (Acid Washing of Laboratory Equipment).

2.4. PS001.1 (Particle Size Reduction).

3. Summary of the Test Method

Based on the information obtained in the "pH001.0 (pH Titration Pretest)" protocol, an acid or base addition schedule is formulated for 11 extracts with final solution pH values between 3 and 12, via addition of HNO_3 or KOH aliquots. The exact schedule is adjusted based on the nature of the material; however, the range of pH values must include the natural pH of the matrix, which may extend the pH domain (e.g., for very alkaline or acidic materials). (Natural pH is defined as the pH, which is obtained when the designated amount of material is contacted with DI water for the designated period of time.) Depending on the natural pH and buffering capacity of the material being tested, HNO_3, and/or KOH may be required to achieve the target pH values. Additionally, if potassium is a COPC, NaOH may be substituted for KOH in this protocol.

Using the schedule, the equivalents of acid or base are added to a combination of deionized (DI) water and the particle size reduced material. The material is particle size reduced to <2 mm, and a sample size of 40 g dry sample is used. [The particle size, sample mass, and contact time shown here represent a typical base case scenario. Alternate sample masses and contact times are required for materials where particle size reduction to <2 mm is either impractical or unnecessary (see accompanying test).] The final liquid-to-solid (LS) ratio is 10 mL extractant/g dry sample, which includes DI water, the added acid or base, and the amount of moisture that is inherent to the waste matrix as determined by moisture content analysis. The 11 extractions are tumbled in an end-over-end fashion at 28 ± 2 rpm for a contact time of 48 h. Following gross separation of the solid and liquid phases by centrifugation or settling, leachate pH measurements are taken and the phases are separated by vacuum filtration through 0.45-μm polypropylene filtration membranes. Analytical samples of the leachates are collected and preserved as appropriate for chemical analysis.

4. Significance and Use

The SR002.1 protocol can be used (1) to create a material-specific titration curve of the acid or base neutralization capacity of the material in contact with varying equivalents of acid or base at a liquid-to-solid ratio of 10 mL/g dry, and (2) to characterize the liquid–solid partitioning equilibrium behavior of COPCs as a function of pH between the pH values of 3 and 12 at a liquid to solid ratio of 10 mL/g dry.

This protocol was modified from the Acid Neutralization Capacity Test (Environment Canada and Alberta Environmental Center 1986) for use with materials having little acid neutralization capacity (e.g., soils or industrial wastes). Size-reduced material and low LS ratio ensure that thermodynamic equilibrium between solid and liquid

phases is obtained within the duration of the protocol for most low solubility constituents (e.g., Pb, As, Cu, Cd). In the case of highly soluble species (e.g., Na, K, Cl), which do not reach saturation prior to complete solubilization of the species from the solid phase, this protocol can be used to measure the release of the available fraction of the total constituent content.

5. Apparatus

5.1. *Extraction Vessel*—a wide-mouth container constructed of high-density polyethylene that does not preclude headspace (e.g., Nalgene #3140-0250 or equivalent). The vessel must have a leak-proof seal that can sustain the end-over-end tumbling and centrifugation required. The container must be of sufficient volume to accommodate both the solid sample and a leachant volume based on a LS ratio of 10 mL extractant/g dry sample. Because centrifugation may be required for gross phase separation, the extraction vessel should be capable of withstanding centrifugation at 4,000 rpm for a minimum of 10 min.

5.2. *Extraction Apparatus*—rotary tumbler capable of rotating the extraction vessels in an end-over-end fashion at a constant speed of 28 ± 2 rpm (e.g., Analytical Testing, Werrington, PA, or equivalent).

5.3. *Filtration Apparatus*—pressure or vacuum filtering apparatus (e.g., Nalgene #300-4000 or equivalent).

5.4. *Filtration Membranes*—0.45-μm pore size polypropylene filtration membrane (e.g., Gelman Sciences GH Polypro #66548, Fisher Scientific, or equivalent).

5.5. *pH Meter*—standard, two point calibration pH meter (e.g., Accumet 20, Fisher Scientific, or equivalent).

5.6. *Adjustable Pipetter*—Oxford Benchmate series or equivalent with disposable tips (delivery range will depend on material neutralization capacity and acid strength).

5.7. *Centrifuge (recommended)*—e.g., RC5C, Sorvall Instruments, Wilmington, DE, or equivalent.

6. Reagents and Materials

6.1. *Reagent Grade Water*—deionized water must be used as the major extractant in this procedure. Deionized water with a resistivity of 18.2 MΩ can be provided by commercially available water deionization systems (e.g., Milli-Q Plus, Millipore Corp., Bedford, MA, or equivalent).

6.2. *2 N Nitric Acid Solution*—prepared by diluting Tracemetal Grade Nitric Acid (Fisher Scientific, or equivalent) with deionized water.

6.3. *1 N Potassium Hydroxide Solution*—reagent Grade (Fisher Scientific, or equivalent).

7. Acid Washing Procedure

Because the concentrations of inorganic constituents in leachates may be very low (i.e., <10 μg/L), all laboratory equipment that comes in contact with the material, the extraction fluid, or the leachant must be rinsed with 10% nitric acid followed by three rinses with DI water to remove residual inorganic deposits following "AW001.0 (Acid Washing of Laboratory Equipment)."

8. Initial Sample Preparation

8.1. *Particle Size Reduction*—depending on the nature of the material, a sufficient mass of the material should be particle size reduced to <2 mm using "PS001.1 (Particle Size Reduction)" protocol.

8.2. *Solids Content Determination*—it is necessary to know the solids content of the material being tested so that appropriate adjustments can be made to conduct the test under a specified LS ratio. Prior to the initiation of the test, a moisture content determination of the "as-received" material must be conducted using ASTM Method D 2261-80, "Standard Method for Laboratory Determination of Water (Moisture) Content of Soil, Rock, and Soil–Aggregate Mixtures." The solids content is calculated as the mass of the dried sample divided by the mass of "as-received" material following Equation (A2-1).

$$SC = \frac{M_{\text{dry}}}{M_{\text{rec}}} \tag{A2-1}$$

where *SC* is the solids content (g dry/g), M_{dry} is the dry sample mass (g dry), and M_{rec} is the mass of the "as-received" material (g).

Table A2-1. Example schedule for acid addition for 40 g dry equivalent mass samples and a moisture content (dry basis) of 0.1 mL/g dry for the "SR002.1 (Alkalinity, Solubility and Release as a Function of pH)" protocol.

Extract no.	End point solution pH	Equivalents of acid to add (mEq/g)	Volume of 2 N HNO_3 or 1 N KOH (mL)	Volume of moisture in sample (mL)	Volume of DI water makeup (mL)
1	12.0	−1.10	44.0	4.0	352.0
2	11.0	−0.75	30.0	4.0	366.0
3	10.0	−0.58	23.2	4.0	372.8
4	9.0	−0.15	6.0	4.0	390.0
5	8.0	−0.09	3.6	4.0	392.4
6	Natural	0.00	0.0	4.0	396.0
7	6.0	0.08	1.6	4.0	394.4
8	5.0	0.12	2.4	4.0	393.6
9	4.0	0.90	18.0	4.0	378.0
10	3.0	1.80	36.0	4.0	360.0
11	2.0	3.10	62.0	4.0	334.0

9. SR002.1 Procedure

The SR002.1 protocol may be conducted only after the equivalents of acid or base required to span the desired pH range are determined from a material specific titration curve as generated by "pH001.0 (pH Titration Pretest)" or equivalent. Because the pretest provides information for acid and base additions at LS of 100 mL/g dry sample, the pH response for the SR002.1 protocol at an LS ratio of 10 mL/g dry sample will be approximate. The variability in end point pH, however, is consistent with the objective of this protocol (i.e., to measure constituent solubility and release over a broad pH range with end points of approximately pH 3 and 12). Table A2-1 shows the example schedule of acid or base additions and DI water make up volume for the SR002.1 protocol generated from the titration information shown in Figure 1 using 40 dry g of sample with a moisture content (dry basis) of 0.1 mL/g dry.

9.1. Place the minimum dry equivalent mass (i.e., 40 g dry sample) into each of eleven high-density polyethylene bottles. The equivalent mass of "as-received" material can be calculated if the solids content is known following Equation (A2-4).

$$M_{rec} = \frac{M_{dry}}{SC} \tag{A2-4}$$

where M_{rec} is the mass of the "as-received" material (g), M_{dry} is the dry equivalent sample mass [i.e., 8 g dry for particle size <2 mm (g dry)], and SC is the solids content of the material (g dry/g).

9.2. Label each bottle with the extraction number or acid addition and add the volume of DI water specified in the schedule for LS ratio makeup (e.g., Table A2-1).

9.3. Add the appropriate volume of acid or base to each extraction using an adjustable pipetter. The required volume of acid or base is specified in the schedule for acid addition (e.g., Table A2-1).

9.4. Tighten the leak-proof lid on each bottle and tumble all extracts in an end-over-end fashion at a speed of 28 ± 2 rpm at room temperature (20 ± 2°C) for 48 h.

9.5 At the conclusion of the agitation period, remove the extraction vessels from the rotary tumbler and clarify the leachates by allowing the bottles to stand for 15 min. Alternately, centrifuge the bottles at 4000 ± 100 rpm for 10 ± 2 min.

9.6. Decant a minimum volume of clear, unpreserved supernatant from each extraction to measure and record the solution pH.

9.7. For each extraction, separate the solid from the remaining liquid by vacuum filtration through a 0.45-μm pore

size polypropylene filtration membrane. The filtration apparatus may be exchanged for a clean apparatus as often as necessary until all liquid has been filtered.

9.8. Collect, preserve, and store the amount of leachate required for chemical analysis.

10. SR002.1 Interpretation

10.1. *pH Titration Curve*—the material response to acid or base addition at LS of 10 mL/g dry can be interpreted if a pH titration curve is generated. Plot the pH of the sample analyzed as a function of the equivalents of acid or base added per dry gram of material. For materials where both acid and base were required, equivalents of base can be presented as opposite sign of acid equivalents (i.e., 5 mEq/g of KOH would correspond to −5 mEq/g of HNO$_3$).

10.2. *"Liquid–Solid Partitioning" (LSP) Curve*—after chemical analysis has been conducted, a constituent LSP curve can be generated for each constituent of concern. The constituent concentration in the liquid phase of each extract is plotted as a function of solution pH. The curve indicates the equilibrium concentration of the constituent of interest at LS of 10 mL/g over a pH range. Additionally, the constituent LSP behavior with pH is indicative of specific constituents speciation in the solid matrix. Figure A2-1 illustrates typical LSP curve behaviors for cationic, amphoteric, and oxyanionic constituents as a function of pH.

The shape of the LSP curve (i.e., general location of maxima/minima) is controlled by the equilibrium between liquid phase constituent (e.g., Pb^{+2}) and solid phase species [e.g., Pb(OH)$_2$ or Pb$_3$(PO$_4$)$_2$] as a function of pH. Also, leachate ionic strength and the presence of complexing (e.g., acetate or chloride ions) or coprecipitating (sulfate or carbonate ions) agents in the leachant solution can influence the LSP curvature and magnitude (Kosson *et al.*, 1996).

At very low pH, the matrix often is broken down by the aggressive leachant and the measured constituent solubility approaches a limiting value (as shown in Fig. A2-1). Because much of the nonsilica-based matrix can be digested at pH values ≈2, the corresponding release in this pH range can represent either the release of the total constituent content or the release of only an operationally defined "available fraction" of the total content. To correlate the release in this pH range to total element analyses, a release-based curve can be developed by multiplying the measured release concentration at each pH value by the LS ratio in L/kg.

11. References

KOSSON, D.S., VAN DER SLOOT, H.A., and EIGHMY, T.T. (1996). An approach for estimating of contaminant release during utilization and disposal of municipal waste combustion residues. *J. Hazard. Mater*. **47,** 43–75.
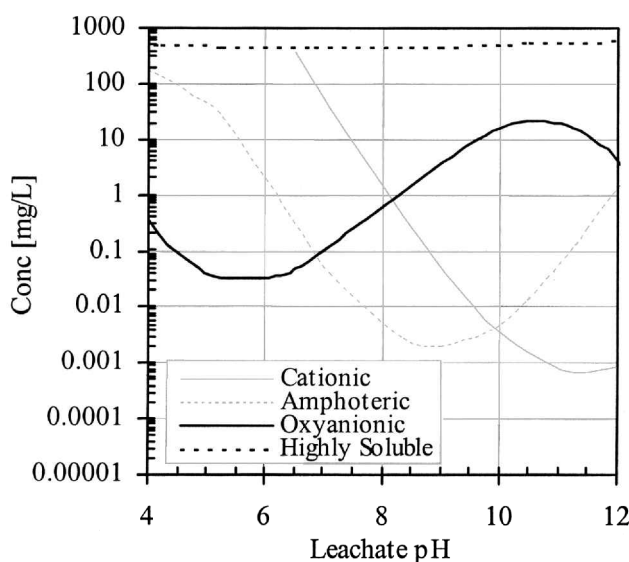

Figure A2-1.   LSP curves of cationic, amphoteric, oxyanionic, and highly soluble species from the SR002.1 protocol.

A.3. SR003.1 (SOLUBILITY AND RELEASE AS A FUNCTION OF LS RATIO)

1. Scope

1.1. This test method is used to determine the effect of low liquid-to-solid ratio on liquid–solid partitioning equilibrium when the solution phase is controlled by the tested material. This is used to approximate initial pore water conditions and initial leachate compositions in many percolation scenarios (e.g., monofills). In this test, the pH and redox conditions are dictated by the sample matrix. The solubility as a function of liquid to solid (LS) ratio can be determined for all "constituents of potential concern" (COPCs) over a range of LS ratios from 10 to 0.5 mL/g dry material.

1.2. This is a characterization protocol (Tier 2b) designed to obtain detailed leachability information.

1.3. This test method is not intended for the characterization of the release of organic constituents.

2. Cited Protocols

2.1. ASTM (1980) "Standard Method for Water (Moisture) Content of Soil, Rock, and Soil–Aggregate Mixtures D 2261-80," Philadelphia, PA: American Society for Testing and Materials.

2.2. AW001.0 (Acid Washing of Laboratory Equipment).

2.3. PS001.1 (Particle Size Reduction).

3. Summary of the Test Method

This protocol consists of five parallel batch extractions over a range of LS ratios (i.e., 10, 5, 2, 1, and 0.5 mL/g dry material), using DI water as the extractant with minimum 40 g dry sample aliquots of material that have been particle size reduced to <2 mm. [The particle size, sample masses, and contact time shown here represent a typical base case scenario. Alternate sample masses and contact times are required for materials where particle size reduction to <2 mm is either impractical or unnecessary (see accompanying text).] Additional material may be required at low LS ratio to provide leachate yield sufficient for analytical methods (Table A3-1). All extractions are tumbled in an end-over-end fashion at 28 ± 2 rpm at room temperature ($20 \pm 2°C$) in leak-proof vessels for 48 h. Following gross separation of the solid and liquid phases by centrifugation or settling, leachate pH and conductivity measurements are taken. The bulk phases are separated by a combination of pressure and vacuum filtration using 0.45-μm polypropylene filter membrane. In all, five leachates are collected, and preserved as appropriate for chemical analysis.

4. Significance and Use

The SR003.1 protocol can be used to provide an estimate of constituent concentration as the extraction LS ratio approaches the bulk porosity of the material. The solution filling the pores of the material (i.e., pore water) locally approaches thermodynamic equilibrium with the different constituents of the material of concern. The resulting pore water solution may be saturated with material constituents, which can result in deviations from ideal dilute solution behavior and activity coefficients significantly different from unity. Estimation of the activity coefficient within the pore water is necessary for accurate estimation of constituent concentration within the pore water and coupled mass transfer rates for leaching. Thus, the use of decreasing LS ratio allows for experimentally approaching the composition of the pore water solution of the material of concern and determining the change in pH and species concentration in comparison to that measured at an LS ratio of 10 mL/g dry as used in the "SR002.1 (Alkalinity, Solubility and Release as a Function of pH)" protocol.

5. Apparatus

5.1. *Extraction Vessel*—a wide-mouth container constructed of plastic, that does not preclude headspace (e.g., Nalgene #3140-0250 or equivalent). The vessel must have a leak-proof seal that can sustain the end-over-end tum-

Table A3-1. Minimum dry equivalent mass as a function of LS ratio recommended for the SR003.2 protocol.

LS 10 mL/g	LS 5 mL/g	LS 2 mL/g	LS 1 mL/g	LS 0.5 mL/g
40 g	40 g	50 g	100 g	200 g

bling and centrifugation required. The container must be of sufficient volume to accommodate both a minimum solid sample mass and a leachant volume based on a maximum LS ratio of 10-mL extractant/g dry sample. The extraction vessel should be capable of withstanding centrifugation at 4000 rpm for minimum of 10 min.

5.2. *Extraction Apparatus*—rotary tumbler capable of rotating the extraction vessels in an end-over-end fashion at constant speed of 28 ± 2 rpm (e.g., Analytical Testing, Werrington, PA, or equivalent).

5.3. *Filtration Apparatus*—filtering apparatus (e.g., Nalgene #300-4000, or equivalent) capable of pressure and vacuum filtration.

5.4. *Filtration Membranes*—0.45-μm pore size polypropylene filtration membrane (e.g., Gelman Sciences GH Polypro #66548, Fisher Scientific, or equivalent).

5.5. *pH Meter*—standard, two point calibration pH meter (e.g., Accumet 20, Fisher Scientific, or equivalent).

5.6. *Graduated Cylinder*—determined by particle size and LS ratio, polymethylpentene (e.g., Nalgene #3663-0100, or equivalent) volume.

5.7. *Centrifuge*—e.g., RC5C, Sorvall Instruments, Wilmington, DE, or equivalent.

6. Reagents and Materials

6.1. *Reagent Grade Water*—deionized water must be used as the major extractant in this procedure. Deionized water with a resistivity of 18.2 MΩ can be provided by commercially available water deionization systems (e.g., Milli-Q Plus, Millipore Corp., Bedford, MA, or equivalent).

7. Acid Washing Procedure

Because the concentrations of inorganic constituents in leachates may be very low (i.e., <10 μg/L), all laboratory equipment that comes in contact with the material, the extraction fluid, or the leachant must be rinsed with 10% nitric acid followed by three rinses with DI water to remove residual inorganic deposits following AW001.0 (Acid Washing of Laboratory Equipment).

8. Initial Sample Preparation

8.1. *Particle Size Reduction*—depending on the nature of the material, a sufficient mass of the material should be particle size reduced to <2 mm using "PS001.1 (Particle Size Reduction)" protocol.

8.2. *Solids Content Determination*—it is necessary to know the solids content of the material being tested so that appropriate adjustments can be made to conduct the test under a specified LS ratio. Prior to the initiation of the test, a moisture content determination of the "as-received" material must be conducted using ASTM Method D 2261-80, "Standard Method for Laboratory Determination of Water (Moisture) Content of Soil, Rock, and Soil–Aggregate Mixtures." The solids content is calculated as the mass of the dried sample divided by the mass of "as received" material following Equation (A3-1).

$$SC = \frac{M_{\text{dry}}}{M_{\text{rec}}} \qquad\qquad\qquad\qquad \text{(A3-1)}$$

where SC is the solids content (g dry/g), M_{dry} is the dry sample mass [g dry], and M_{rec} is the mass of the "as-received" material (g).

9. SR003.1 Procedure

9.1. Place the minimum dry equivalent mass required for each LS ratio (Table A3-1) into each of five high-density polyethylene bottles. The equivalent mass of "as-received" material can be calculated if the solids content is known following Equation (A3-2).

$$M_{\text{rec}} = \frac{M_{\text{dry}}}{SC} \qquad\qquad\qquad\qquad \text{(A3-2)}$$

where M_{rec} is the mass of the "as-received" material (g), M_{dry} is the dry equivalent sample mass (see Table A3-1) (g dry), and *SC* is the solids content of the material (g dry/g).

9.2. Measure out the appropriate volume of DI water in a graduate cylinder for each of the following LS ratios— 10, 5, 2, 1, and 0.5 mL/g dry equivalent mass. For a dry material, this volume will be the mass of the aliquot

multiplied by the desired LS ratio. However, if the material has high moisture content (e.g., >5%), the volume of water contained in the sample should be subtracted from the volume of DI water to be added.

9.3. Add the DI water to the solid material and tighten the leak-proof lid.

9.4. Tighten the leak-proof lid on each bottle and tumble all extracts in an end-over-end fashion at a speed of 28 ± 2 rpm at room temperature (20 ± 2°C) for 48 h.

9.5. Remove the extraction vessel from the rotary tumbler at the conclusion of the agitation period.

9.6. Clarify the leachates by allowing the bottles to stand for 15 min. Alternately, centrifuge the bottles at 4000 ± 100 rpm for 10 ± 2 minutes.

9.7. Decant a minimum volume of clear, unpreserved supernatant to measure the solution pH.

9.8. Separate the solid from the remaining liquid by a combination of pressure and vacuum filtration through a 0.45-μm pore size polypropylene filtration membrane. A nonreactive gas (e.g., nitrogen or argon) should be used for pressure filtration. The filtration apparatus may be exchanged for a clean apparatus as often as necessary until all liquid has been filtered.

9.9. Collect, preserve, and store the amount of leachate required for chemical analysis.

10. SR003.1 Interpretation

The filtered extracts are analyzed for common ionic strength-contributing cations (i.e., sodium, potassium, calcium) and any other constituents of interest. Conductivity, pH, and concentrations of constituents of concern as a function of the liquid to solid ratio then are extrapolated to the liquid to solid ratio for the pore water within the matrix. The liquid-to-solid ratio for the pore water is defined by the porosity of the matrix as:

$$LS = \frac{\epsilon}{\rho_{dry}} \tag{A3-3}$$

where LS is the liquid-to-solid ratio on a dry basis (mL/g dry), ϵ is the porosity (cm^3/cm^3) estimated by measuring the water absorption capacity of the matrix, and ρ_{dry} is the density on a dry basis (g dry/cm^3).

The resulting concentrations of sodium, potassium, and hydroxide (i.e., pH) then are used to estimate the pore water ionic strength and activity coefficients.

A.4. MT001.1 (MASS TRANSFER RATES IN MONOLITHIC MATERIALS)

1. Scope

1.1. This protocol assesses the release rate of "constituents of potential concern" (COPCs) from monolithic materials under mass transfer-controlled release conditions. These conditions occur when the mode of water contact with the solid material results in a flow around a structure with low permeability (e.g., cement treated wastes, capped granular fills, or compacted granular material).

1.2. This test method is not intended for the characterization of the release behavior of organic constituents.

2. Cited Protocols

2.1. ASTM (1980) "Standard Method for Water (Moisture) Content of Soil, Rock, and Soil–Aggregate Mixtures D 2261-80," Philadelphia, PA: American Society for Testing and Materials.

2.2. U.S. Army Corps of Engineers (1970) Engineering Manual. "Engineering and Design: Laboratory Soils Testing." *EM 1110-2-1906*, Washington, DC: Office of the Chief of Engineers.

2.3. AW001.0 (Acid Washing of Laboratory Equipment).

3. Summary of the Test Method

The MT001.1 (Mass Transfer Rates in Monolithic Materials) protocol consists of tank leaching of continuously water-saturated monolithic material with periodic renewal of the leaching solution. The vessel and sample dimensions are chosen so that the sample is fully immersed in the leaching solution. Cylinders of 2-cm minimum diameter and 4-cm minimum height or 4-cm minimum cubes are contacted with DI water using a liquid to surface area ratio of 10 mL of DI water for every cm^2 of exposed solid surface area. Leaching solution is exchanged with fresh

DI water at predetermined cumulative times of 2, 5 and 8 h, 1, 2, 4, and 8 days. (This schedule may be extended for additional extractions to provide more information about longer term release. The recommended schedule extension would be additional cumulative times 14 days, 21 days, 28 days, and every 4 weeks thereafter as desired.) This schedule results in seven leachates with leaching intervals of 2, 3, 3, and 16 h, 1, 2, and 4 days. At the completion of each contact period, the mass of the monolithic sample after being freely drained is recorded to monitor the amount of leachant absorbed into the solid matrix. The solution pH and conductivity for the leachate is measured for each time interval. A leachate sample is prepared for chemical analysis by vacuum filtration through a 0.45-μm pore size polypropylene filtration membrane and preservation as appropriate. Leachate concentrations are plotted as a function of time along with the analytical detection limit and the equilibrium concentration determined from SR002.1 protocol at the extract pH for quality control. Cumulative release and flux as a function of time for each constituent of interest are plotted and used to estimate mass transfer parameters (i.e., observed diffusivity).

4. Significance and Use

The objective of the MT001.1 protocol is to measure the rate of COPC release from a monolithic material (e.g., solidified waste form or concrete matrix) under leaching conditions where the rate of mass transfer through the solid phase controls constituent release. These conditions simulate mechanisms that occur when water (e.g., infiltration or groundwater) is diverted to flow around a relatively impermeable material (e.g., solidified waste forms, road base material, or capped granular fills). Results of this test are used to estimate intrinsic mass transfer parameters (e.g., observed diffusivities for COPCs) that are then used in conjunction with other testing results and assessment models to estimate release. Results of the MT001.1 protocol reflect both physical and chemical interactions within the tested matrix, thus requiring additional test results for integrated assessment. Although the recommended method is derivative of ANS 16.1 (ANS 1986), a leachability index is not assumed nor used as a decision criterion.

5. Apparatus

5.1. Extraction Vessel—a polypropylene container with an opening large enough so that the monolith can be easily removed and replaced. The container must also have an air-tight cover to minimize the exposure to carbon dioxide, which can lead to carbonate formation in some highly alkaline matrices.

5.2. *Monolith Holder*—a mesh or structured holder constructed of an inert material to leachate constituents and acid washing liquids. At least 98% of the monolith surface area should be exposed to the leachant. Also, the holder must orient the monolith in the center of the leaching vessel so that there is an approximately equal amount of leachant opposing every surface. A schematic of one such design for 10-cm diameter by 10-cm cylindrical samples is presented in Figure A4-1. The dimension of this apparatus may be scaled as appropriate for sample size.

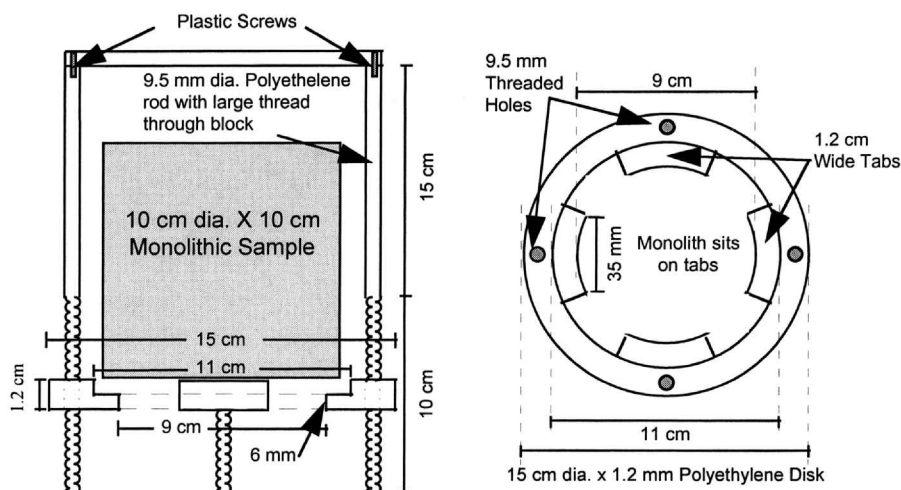5.3. *Filtration Apparatus*—pressure or vacuum filtering apparatus (e.g., Nalgene #300-4000, or equivalent).

Figure A4-1.   Design schematic for monolithic sample holder for MT001.1 (Mass Transfer in Monolithic Materials) protocol.

5.4. *Filtration Membranes*—0.45-μm pore size polypropylene filtration membrane (e.g., Gelman Sciences GH Polypro, Fisher Scientific #66548, or equivalent).

5.5. *pH Meter*—standard, two point calibration pH meter (e.g., Accumet 20, Fisher Scientific, or equivalent).

5.6. *Beaker*—100-mL borosilicate glass (e.g., Fisher Brand, or equivalent).

6. Reagents and Materials

6.1 *Reagent Grade Water*—deionized water must be used as the major extractant in this procedure. Deionized water with a resistivity of 18.2 MΩ can be provided by commercially available water deionization systems (e.g., Milli-Q Plus, Millipore Corp., Bedford, MA, or equivalent).

7. Acid Washing Procedure

Because the concentrations of inorganic constituents in leachates may be very low (i.e., <10 μg/L), all laboratory equipment that comes in contact with the material, the extraction fluid, or the leachant must be rinsed with 10% nitric acid followed by three rinses with DI water to remove residual inorganic deposits following AW001.0 (Acid Washing of Laboratory Equipment).

8. Initial Sample Preparation

8.1. *Preparation of Monolithic Samples*—the surface area of the monolithic sample must be known to estimate constituent release from the test sample in the MT001.1 protocol. A representative sample of existing monolithic materials must be obtained by coring or some other nondestructive method. Cylinders of 2-cm minimum diameter and 4-cm minimum height or 4-cm minimum cubes are recommended.

8.2. *Moisture Determination*—it is necessary to know the moisture content of the material being tested so that the release of constituents can be normalized to the dry equivalent mass of the monolith. This adds flexibility to the leaching characterization approach by allowing for comparison among treatment options of varying moisture contents. Because moisture content procedures tend to alter the chemical and physical properties of the solid phase, an additional sample must be prepared in exactly the same manner as the test sample to use for moisture determination. Alternately, determination of moisture content may be taken using material samples segregated during gross particle size reduction following the "PS001.0 (Particle Size Reduction to <300 μm, <2 mm or <5 mm)" protocol. Moisture determination of the solid matrix must be conducted using ASTM Method D 2261-80, "Standard Method for Laboratory Determination of Water (Moisture) Content of Soil, Rock, and Soil–Aggregate Mixtures."

9. MT001.0 Procedure

This protocol is a dynamic tank leaching procedure with leachant exchanges at cumulative leaching times of 2, 5, and 8 h, 1, 2, 4, and 8 days. This schedule results in seven leachates with leaching intervals of 2, 3, 3, and 16 h, 1, 2, and 4 days. The leachant is DI water and the pH of each leachate is measured.

9.1. *Specimen Measurements*

    9.1.1. Measure and record the dimensions (i.e., diameter and height for a cylinder; length, width, and depth for a parallelepiped) of the monolithic specimen for surface area calculation.

    9.1.2. Measure and record the mass of the specimen. This value is monitored for each leachant exchange.

    9.1.3. Place the specimen in the monolith holder, if a holder is used.

    9.1.4. Measure and record the mass or the specimen and holder, if applicable.

9.2. *Leachant Exchange*

    9.2.1. Place the mesh (if a mesh is used instead or a holder), in a clean leaching vessel.

    9.2.2. Fill the clean leaching vessel with the required volume of DI water using a liquid to surface area ratio of 10 mL of DI water for every cm^2 of exposed solid surface area.

    9.2.3. Gently place the specimen or the specimen and holder in the leaching vessel so that the leachant is evenly distributed around the specimen. Submersion should be gentle enough that the physical integrity of the monolith is maintained and wash-off is minimized.

    9.2.4. Cover the leaching vessel with the air-tight lid.

9.2.5. By repeating Steps 9.2.1–9.2.2 at the end of the leaching interval, prepare a fresh leachant in a new leaching vessel.

9.2.6. Remove the specimen or the specimen and holder from the vessel. Drain the liquid from the surface of the specimen into the leachate for approximately 20 s.

9.2.7. Measure and record the mass of the specimen or the mass of the specimen and holder. The difference in mass between measurements is an indication of the potential sorption of leachant by the matrix. In the case where a holder is used, moisture will condense on the holder as the leaching intervals increase in duration and sample sorption may not be evident.

9.2.8. Place the specimen or the specimen and holder into the clean leaching vessel of new leachant prepared in Step 9.2.2.

9.2.9. Cover the clean leaching vessel with the air-tight lid.

9.2.10. Decant 25–50 mL of leachate into a 100-mL beaker.

9.2.11. Measure and record the pH of the decanted leachate.

9.2.12. Filter the remaining leachate through a 0.45-μm polypropylene membrane.

9.2.13. Collect and preserved enough leachate for chemical analysis.

9.2.14. Repeat the leachate exchange procedure (Steps 9.2.1–9.2.14) until all seven leachants are collected.

10. MT001.0 Interpretation

10.1. *Mass Transfer Coefficients*—interpretation of the release of constituents using the "MT001.0 (Mass Transfer Rates in Monolithic Materials)" protocol is illustrated using the bulk diffusion model. Other models that may also be used to determine mass transfer coefficients and tortuosity values include the Shrinking Unreacted Core model (Hinsenveld and Bishop, 1996) and the Coupled Dissolution-Diffusion model (Sanchez, 1996). These models incorporate chemical release parameters into the model to better estimate release mechanisms and predictions.

At the conclusion of the MT001.0 protocol, the interval mass released is calculated for each leaching interval as:

$$M_{ti} = \frac{C_i V_i}{A} \tag{A4-1}$$

where M_{t_i} is the mass released during leaching interval i (mg/m^2), C_i is the constituent concentration in interval i (mg/L), V_i is the leachant volume in interval i (L), and A is the specimen surface area exposed to the leachant (m^2).

An observed diffusivity of COPCs can be determined using the logarithm of the cumulative release plotted vs. the logarithm of time. In the case of a diffusion–control mechanism, this plot is expected to be a straight line with a slope of 0.5. An observed diffusivity can then be determined for each leaching interval where the slope is 0.5 ± 0.15 by (de Groot and van der Sloot, 1992):

$$D_i^{\mathrm{obs}} = \pi \left(\frac{M_{t_i}}{2 \, \rho \, C_0 \, (\sqrt{t_i} - \sqrt{T_{i-1}})} \right)^2 \tag{A4-2}$$

where D_i^{obs} is the observed diffusivity of the species of concern for leaching interval i (m^2/s), M_{t_i} is the mass released during leaching interval i (mg/m^2), t_i is the contact time after leaching interval i (s), t_{i-1} is the contact time after leaching interval $i-1$ (s), C_0 is the Initial leachable content (i.e., available release potential) (mg/kg), and ρ is the sample density (kg/m^3).

The overall observed diffusivity is then determined by taking the average of the interval observed diffusivities. Only those interval mass transfer coefficients corresponding to leaching intervals with slopes between 0.35 and 0.65 are included in the overall average mass transfer coefficient (IAWG, 1997).

10.2. *Matrix Tortuosity*—tortuosity is a measure of the physical retention in the matrix and is a matrix-specific property. The matrix tortuosity reflects the extended path length of a diffusing ion in the pore structure of a matrix relative to a straight path through the matrix. Typically, the mass transfer release of noninteractive components, or tracers, is measured and observed interval mass transfer coefficients are compared to the tracer molecular diffusivity in aqueous solutions as shown in Equation (A4-4).

$$\tau = \frac{D^{\mathrm{mol}}}{D^{\mathrm{obs}}} \tag{A4-4}$$

where τ is the the matrix physical retention, or tortuosity ($-$), D^{mol} is the molecular diffusion coefficient in aqueous solution (m^2/s), and D^{obs} is the observed diffusion coefficient in the matrix (m^2/s).

Sodium or chloride is normally selected as tracer elements under the assumption that these elements do not react with the matrix being evaluated. The matrix tortuosity should be calculated as the average of interval tortuosity values subject to the same interval slope criteria (0.35—0.65) pertaining to mass transfer coefficients.

11. References

DE GROOT, G.J., and VAN DER SLOOT, H.A. (1992). Determination of leaching characteristics of waste materials leading to environmental product certification. In: T.M. Gillam and C.C. Wiles, Eds., *Solidification and Stabilization of Hazardous, Radioactive, and Mixed Wastes, 2nd Volume, ASTM STP 1123*. Philadelphia, PA: American Society for Testing and Materials, pp. 149–170.

HINSENVELD, M., and BISHOP, P.L. (1996). Use of the shrinking core/exposure model to describe the leachability from cement stabilized wastes. In T.M. Gilliam and C.C. Wiles, Eds., *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes, 3rd Volume, ASTM STP 1240*, Philadelphia, PA: American Society for Testing and Materials.

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SANCHEZ, F. (1996). Etude de la lixiviation de milieux poreux contenant des espèces solubles: Application au cas des déchets solidifiés par liants hydrauliques. Doctoral Thesis, Lyon, France: Institut National des Sciences Appliquées de Lyon.

A.5. MT002.1 (MASS TRANSFER RATE IN GRANULAR MATERIALS)

1. Scope

1.1. This protocol assesses the release rate of "constituents of potential concern" (COPCs) from compacted granular matrices under mass transfer-controlled release conditions. These conditions occur when the mode of water contact with the solid material results in a flow around a material structure (e.g., capped granular fills, or low permeability compacted granular material).

1.2. This test method is not intended for the characterization of the release behavior of organic constituents.

2. Cited Protocols

2.1. ASTM (1978) "D 1557. Standard Method for Moisture-Density Relations of Soils and Soil-Aggregate Mixtures Using 10 lb. Rammer and 18 in. Drop," Philadelphia, PA: American Society for Testing and Materials.

2.2. ASTM (1980) "D 2261-80. Standard Method for Water (Moisture) Content of Soil, Rock, and Soil–Aggregate Mixtures," Philadelphia, PA: American Society for Testing and Materials.

2.4. U.S. Army Corps of Engineers (1970) Engineering Manual. "Engineering and Design: Laboratory Soils Testing." *EM 1110-2-1906*, Washington, DC: Office of the Chief of Engineers

2.5. AW001.0 (Acid Washing of Laboratory Equipment).

3. Summary of the Test Method

The MT002.0 (Mass Transfer Rates in Compacted Granular Materials) consists of tank leaching of continuously water-saturated compacted granular material with intermittent renewal of the leaching solution. This test is used when a granular material is expected to behave as a monolith because of compaction during field placement. An unconsolidated or granular material, size-reduced to <2 mm is compacted into molds using modified Proctor Compactive Effort (ASTM Method D 1557 "Standard Method for Moisture–Density Relations of Soils and Soil–Aggregate Mixture using 10 lb. Rammer and 18 in. Drop"). (The particle size reduction and cylindrical matrix diameter specified represents a base case scenario. Change in the particle size specification requires alteration of the compacted sample diameter for a cylindrical matrix such that the matrix diameter is 10 times the maximum particle diameter.) A 10-cm diameter cylindrical mold is used, and the sample is packed to a depth of 10 cm. The mold and sample are immersed in DI such that only the surface area of the top face of the sample contacted the leaching medium. The

leachant is refreshed with an equal volume of DI using a liquid to surface area ratio of 10 mL/cm^2 (i.e., LS of 10 cm) at cumulative times of 2, 5, and 8 h, 1, 2, 4, and 8 days. (This schedule may be extended for additional extractions to provide more information about longer term release. The recommended schedule extension would be additional cumulative times 14 days, 21 days, 28 days, and every 4 weeks thereafter as desired.) This schedule results in seven leachates with leaching intervals of 2, 3, 3, and 16 hours, 1, 2, and 4 days. The solution pH and conductivity for the leachate is measured for each time interval. A leachate sample is prepared for chemical analysis by vacuum filtration through a 0.45-μm pore size polypropylene filtration membrane and preservation as appropriate. Leachate concentrations are plotted as a function of time along with the analytical detection limit and the equilibrium concentration determined from SR002.1 protocol at the extract pH for purposes of quality control. Cumulative release and flux as a function of time for each constituent of interest are plotted and used to estimate mass transfer parameters (i.e., observed diffusivity).

4. Significance and Use

The objective of the MT002.1 protocol is to measure the rate of COPC release from compacted granular materials under leaching conditions where the rate of mass transfer through the solid phase can control constituent release. These conditions simulate mechanisms that occur when water (e.g., infiltration or groundwater) is diverted to flow around a relatively impermeable material (e.g., compacted granular fills). Results of this test are used to estimate intrinsic mass transfer parameters (e.g., observed diffusivities for COPCs) that are then used in conjunction with other testing results and assessment models to estimate release.

5. Apparatus

5.1. *Extraction Vessel*—a polypropylene container with an opening large enough so that the monolith can be easily removed and replaced (e.g., Cole-Parmer #AP-06083-15 or equivalent). The container must also have an airtight cover to minimize the exposure to carbon dioxide, which can lead to carbonate formation in some highly alkaline matrices.

5.2. *Specimen Mold*—a 10-cm diameter by 10-cm high cylindrical mold constructed of an inert material to leachate constituents and acid washing liquids (e.g., MA Industries, Inc., Peachtree City, GA, or equivalent). It must be constructed so that the exposed surface area of the test specimen is only one circular face of the mold. If necessary, 3-mm diameter drain holes may be cut into the mold to aid in drainage of leachate from the mold. These holes should be placed at least 10 cm above the bottom of the mold. A schematic of one such design is presented in Figure A5-1.

5.3. *Filtration Apparatus*—pressure or vacuum filtering apparatus (e.g., Nalgene #300-4000 or equivalent).

5.4. *Filtration Membranes*—0.45-μm pore size polypropylene filtration membrane (e.g., Gelman Sciences GH Polypro #66548, Fisher Scientific, or equivalent).

5.5. *pH Meter*—standard, two point calibration pH meter (e.g., Accumet 20, Fisher Scientific, or equivalent).

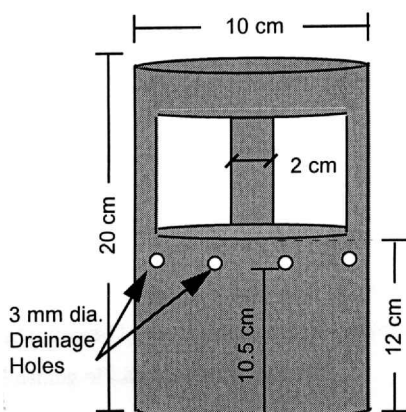5.6. *Beaker*—100 mL, borosilicate glass (e.g., Fisherbrand or equivalent).

Figure A5-1.   Design schematic for compacted sample mold for MT002.1 (Mass Transfer in Granular Materials) protocol.

6. Reagents and Materials

6.1. *Reagent Grade Water*—deionized water must be used as the major extractant in this procedure. Deionized water with a resistivity of 18.2 MΩ can be provided by commercially available water deionization systems (e.g., Milli-Q Plus, Millipore Corp., Bedford, MA, or equivalent).

7. Acid Washing Procedure

Because the concentrations of inorganic constituents in leachates may be very low (i.e., <10 μg/L), all laboratory equipment that comes in contact with the material, the extraction fluid, or the leachant must be rinsed with 10% nitric acid followed by three rinses with DI water to remove residual inorganic deposits following "AW001.0 (Acid Washing of Laboratory Equipment)."

8. Initial Sample Preparation

8.1. *Optimum Moisture Content*—optimum moisture content refers to the amount of moisture [fractional mass of water (g water/g dry material)] in the granular sample that is present at the optimum packing density (g dry material/cm^3). This density is defined and the determination described in ASTM Method D 1557 "Standard Method for Moisture-Density Relations of Soils and Soil–Aggregate Mixtures Using 10 lb. Rammer and 18 in. Drop." Modifications of this standard method are used as described below. The optimum moisture content of the material is determined using a preliminary test consisting of determining the dry density of the compacted material as a function of varying water contents. For this purpose, ca. 100 g of "as-received" material compacted in a 4.8-cm diameter mold are used. Three consecutive layers of materials are compacted 25 times using a 1 kg (2 lb) hammer and 45 cm (18 in) drop [modifications of the Proctor Compactive Effort (ASTM D 1557 "Standard Method for Moisture-Density Relations of Soils and Soil–Aggregate Mixtures Using 10 lb. Rammer and 18 in. Drop")]. The height and weight of the resulting compacted material is measured. A known amount of water is then added and mixed with the same material sample and the same procedure as for the "as-received" material is followed. This step is repeated several times, and then a curve of the dry density vs. the water content, expressed as a percent of the dry mass of material, is drawn. This curve is parabolic, with the maximum indicating the optimum water content. It is important that the granular material be compacted at optimum moisture content to obtain packing densities that approximate field conditions.

8.2. *Moisture Determination*—prior to the initiation of the test, a moisture determination of the compacted granular matrix must be conducted using ASTM Method D 2261-80, "Standard Method for Laboratory Determination of Water (Moisture) Content of Soil, Rock, and Soil–Aggregate Mixtures." The moisture content determination also may be conducted on the unconsolidated bulk material used for the compaction at the optimum moisture content.

9. MT002.1 Procedure

The MT002.1 procedure is a dynamic tank leaching procedure with leachant exchanges at predetermined cumulative times of 2, 5, and 8 h, 1, 2, 4, and 8 days. This schedule results in seven leachates with leaching intervals of 2, 3, 3, and 16 h, 1, 2, and 4 days. The leachant is DI water and the pH of each leachate is recorded.

9.1. *Preparation of Test Specimens*

    9.1.1. Measure and record the mass of a clean sample mold.

    9.1.2. Using the method described below, compact the granular material at its optimum moisture content into the mold to a minimum height of 10 cm. It is recommended that the compacted height be slightly under the drainage holes for best drainage of the sample.

            Compaction technique: three consecutive layers of material are compacted 25 times using a 1 kg (2 lb) hammer and 45-cm (18 in) drop [modifications of the Proctor Compactive Effort (ASTM D 1557 "Standard Method for Moisture–Density Relations of Soils and Soil–Aggregate Mixtures Using 10 lb. Rammer and 18 in. Drop")].

    9.1.3. Measure and record the mass of the sample mold and compacted sample. The difference in this measurement and the empty mold mass (Step 9.1.1) is recorded as the mass of granular material at optimum moisture. This value is monitored at the end of each leaching interval as an indication of the mass of leachant that is sorbed into the matrix.

9.1.4. Measure and record the height of the compacted matrix by measuring the outer height of the mold to the rim and subtracting the inside depth from the rim to the matrix.

9.2. *Leachant Exchange*

9.2.1. Fill a clean leaching vessel with 1000 mL of DI water.

9.2.2. At the beginning of the first leaching interval, there is no recovered leachate. The sample and mold are gently placed in the leaching vessel so that the leachant is evenly distributed around the sample. Submersion should be gentle enough that the physical integrity of the monolith is maintained.

9.2.3. Cover the leaching vessel with the air-tight lid.

9.2.4. At the end of the leaching interval, prepare a fresh leachant in a new leaching vessel (Step 9.2.1).

9.2.5. Remove the sample and mold from the vessel. Drain the leachate from the surface of the specimen into the leachate for approximately 20 s.

9.2.6. Measure and record the mass of the sample and mold. The difference in mass between interval measurements is an indication of the potential sorption of leachant by the matrix.

9.2.7. Place the sample and holder into the clean leaching vessel of new leachant.

9.2.8. Cover the clean leaching vessel with the air-tight lid.

9.2.9. Decant 25–50 mL of leachate into a 100-mL beaker.

9.2.10. Measure and record the pH of the decanted leachate.

9.2.11. Filter at least 500 mL of the remaining leachate through a 0.45-mm polypropylene membrane. After filtration, the remaining leachate is discarded.

9.2.12. Collect and preserved enough leachate for chemical analysis.

9.2.13. Repeat the leachate exchange procedure (Steps 9.2.1–9.2.12) until all seven leachants are collected.

10. MT002.1 Interpretation

10.1. *Mass Transfer Coefficients*—interpretation of the release of constituents using the MT002.0 (Mass Transfer Rates in Granular Materials) protocol is illustrated using the bulk diffusion model. Other models that may also be used to determine mass transfer coefficients and tortuosity values include the Shrinking Unreacted Core model (Hinsenveld and Bishop, 1996) and the Coupled Dissolution/Diffusion model (Sanchez, 1996). These models incorporate chemical release parameters into the model to better estimate release mechanisms and predictions.

At the conclusion of the MT001.0 protocol, the interval mass released is calculated for each leaching interval as:

$$M_{t_i} = \frac{C_i V_i}{A} \tag{A5-1}$$

where M_{t_i} is the mass released during leaching interval i (mg/m^2); C_i is the constituent concentration in interval i (mg/L), V_i is the leachant volume in interval i (L), and A is the specimen surface area exposed to the leachant (m^2).

An observed diffusivity of COPCs can be determined using the logarithm of the cumulative release plotted vs. the logarithm of time. In the case of a diffusion-control mechanism, this plot is expected to be a straight line with a slope of 0.5. An observed diffusivity can then be determined for each leaching interval where the slope is 0.5 ± 0.15 by (de Groot and van der Sloot, 1992):

$$D_i^{\text{obs}} = \pi \left(\frac{M_{t_i}}{2 \, \rho \, C_0 \, (\sqrt{t_i} - \sqrt{t_{i-1}})} \right)^2 \tag{A5-2}$$

where D_i^{obs} is the observed diffusivity of the species of concern for leaching interval i (m^2/s), M_{t_i} is the mass released during leaching interval i (mg/m^2), t_i is the contact time after leaching interval i (s), t_{i-1} is the contact time after leaching interval $i-1$ (s), C_0 is the Initial leachable content (i.e., available release potential) (mg/kg), and ρ is the sample density (kg/m^3).

The overall observed diffusivity is then determined by taking the average of the interval observed diffusivities. Only those interval mass transfer coefficients corresponding to leaching intervals with slopes between 0.35 and 0.65 are included in the overall average mass transfer coefficient (IAWG, 1997).

10.2. *Matrix Tortuosity*—tortuosity is a measure of the physical retention in the matrix and is a matrix-specific property. The matrix tortuosity reflects the extended path length of a diffusing ion in the pore structure of a matrix

relative to a straight path through the matrix. Typically, the mass transfer release of noninteractive components, or tracers, is measured and observed interval mass transfer coefficients are compared to the tracer molecular diffusivity in aqueous solutions as shown in Equation (A4-4).

$$\tau = \frac{D^{\text{mol}}}{D^{\text{obs}}} \qquad (A5-3)$$

where τ is the the matrix physical retention, or tortuosity ($-$), D^{mol} is the molecular diffusion coefficient in aqueous solution (m^2/s), and D^{obs} is the the observed diffusion coefficient in the matrix (m^2/s).

Sodium or chloride is normally selected as tracer elements under the assumption that these elements do not react with the matrix being evaluated. The matrix tortuosity should be calculated as the average of interval tortuosity values subject to the same interval slope criteria (0.35–0.65) pertaining to mass transfer coefficients.

11. References

DE FROOT, G.J., and VAN DER SLOOT, H.A. (1992). Determination of leaching characteristics of waste materials leading to environmental product certification. In: T.M. Giliam and C.C. Wiles, Eds., *Solidification and Stabilization of Hazardous, Radioactive, and Mixed Wastes, 2nd Volume, ASTM STP 1123*. Philadelphia, PA: American Society for Testing and Materials, pp. 149–170.

HINESENVELD, M., and BISHOP, P.L. (1996). Use of the shrinking core/exposure model to describe the leachability from cement stabilized wastes." In T.M. Gilliam and C.C. Wiles, Eds., *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes, 3rd Volume, ASTM STP 1240*, Philadelphia, PA: American Society for Testing and Materials.

IAWG. (1997). *Municipal Solid Waste Incinerator Residues*. Amsterdam: Elsevier Science Publishers.

SANCHEZ, F. (1996). Etude de la lixiviation de milieux poreux contenant des espèces solubles: Application au cas des déchets solidifiés par liants hydrauliques. Doctoral Thesis, Lyon, France: Institut National des Sciences Appliquées de Lyon.

A.6. pH001.0 (PH TITRATION PRETEST)

1. Scope

1.1. This protocol is used to generate a material-specific pH titration curve of a solid material at a liquid–solid (LS) ratio of 100 mL/g dry sample. This titration curve is used to formulate an acid and base addition schedule for the "SR002.1 (Alkalinity, Solubility and Release as a Function of pH)" protocol.
1.2. This protocol is not intended for determination of pH titration data for organic matrices.

2. Cited Protocols

2.1. ASTM (1980) "D 2261-80 Standard Method for Determination of Water (Moisture) Content of Rock, Soil and Soil–Aggregates mixtures," Philadelphia, PA: American Society for Testing and Materials.
2.2. SR002.1 (Alkalinity, Solubility and Release as a Function of pH).
2.3. AW001.0 (Acid Washing for Laboratory Equipment).
2.4. PS001.1 (Particle Size Reduction).

3. Summary of the Method

This protocol is used to obtain a material-specific titration curve between the pH values of 2 and 12. From this titration curve, the required equivalents of acid or base to obtain endpoint pH values are determined for addition to DI water extractions in the "SR002.1 (Alkalinity, Solubility and Release as a Function of pH)" protocol. All procedures are conducted at room temperature (20 $\pm$ 2°C) and at a LS ratio of 100 mL/g dry sample on material that has been size reduced to <2 mm using "PS001.1 (Particle Size Reduction)" protocol. In the pH001.0 protocol, a minimum equivalent sample mass of 8 g dry sample is used. The natural pH of the appropriate sample mass of aliquot of material in DI water at an LS ratio of 100 mL/g dry sample is measured in a borosilicate glass beaker using a pH meter. (Natural pH is defined as the pH, which is obtained when the designated amount of material is contacted with DI water for the designated period of time.) The natural pH of the material is used to determine if acid (base) is required to lower (raise) the solution pH in order to cover the range from pH 3 to 12.

Next, a series of 100- to 500-μL aliquots of acid are added to this beaker containing the minimum sample mass (i.e., 8 g dry equivalent mass) and DI water at a LS ratio of 100 mL/g. Nitric acid is used to lower the solution pH. The volume of acid added will depend on the buffering capacity of the material. For each addition, the solution pH is measured after 20–30 min of stirring using a magnetic stirrer followed by 5 min of settling. The cumulative acid addition and the solution pH are monitored for each addition until the desired acidic pH range is covered. The aliquot addition procedure is repeated on a new sample aliquot using 100- to 500-μL aliquots of base, if required, until the entire pH range from values of 3 to 12 is covered. The use of potassium hydroxide or sodium hydroxide to raise the solution pH should be based on consideration of the constituents of interest (i.e., if potassium is a constituent of concern, NaOH must be used in the titration).

From the data collected by addition of acid and/or base, a titration curve showing the pH response as a function of the equivalents of acid or base added per dry gram of sample is generated. Equivalents of base are presented as negative equivalents of acid (i.e., 1 mEq/g dry KOH equals -1 mEq/g dry HNO_3). A schedule of volumetric acid or base additions and extraction media makeup volumes is created for the SR002.1 (Alkalinity, Solubility and Release as a Function of pH) protocol.

4. Significance and Use

Because the release of inorganic constituents is often controlled by liquid phase pH, the end point pH (i.e., the pH of the leachate after the desired contact time) is a critical parameter, which must be controlled, in many leaching protocols. The final pH of the liquid phase is a result of the neutralization, or titration, of the alkalinity in the material by an acid or a base. In batch extraction procedures designed to challenge the material at specific pH target values (e.g., SR002.1 protocol), leachate pH may be controlled by the addition of predetermined equivalents of acid or base according to the acid/base addition schedule and material-specific titration curve as provided by pH001.0 (pH Titration Pretest).

5. Apparatus

5.1. *Beaker*—400 mL borosilicate glass (e.g., Fisher Brand, or equivalent).
5.2. *Magnetic Stirring Bar*—25 mm × 9.5 mm dia. Teflon coated (e.g., Fisherbrand #09-311-9, or equivalent).
5.3. *Magnetic Stirrer*—e.g., Barnstead/Thermolyne S46725, or equivalent.
5.6. *Adjustable Pipetter*—100–1,000 μL Oxford Benchmate, or equivalent, with disposable tips.

6. Reagents

6.1. *Reagent Grade Water*—DI water must be used as the major extractant in this procedure. DI water with a resistivity of 18.2 MΩ can be provided by commercially available water deionization systems (e.g., Milli-Q Plus, Millipore Corp., Bedford, MA, or equivalent).
6.2. *2 N Nitric Acid Solution*—prepared by diluting Tracemetal Grade Nitric Acid (e.g., Fisher Scientific, or equivalent) with deionized water.
6.3. *1 N Potassium Hydroxide Solution*—Reagent grade (e.g., Fisher Scientific, or equivalent).

7. Acid Washing Procedure

Because the concentrations of inorganic constituents in leachates may be very low (i.e., <10 μg/L), all laboratory equipment that comes in contact with the material, the extraction fluid, or the leachant must be rinsed with 10% nitric acid followed by three rinses with DI water to remove residual inorganic deposits following AW001.0 (Acid Washing of Laboratory Equipment).

8. pH001.0 Procedure

The pH001.0 protocol consists of three sections used to (1) measure the natural pH of a size reduced material in DI water at a LS ratio of 100 mL/g dry sample, (2) determine the pH titration behavior of the material to addition of 2 N nitric acid or 1 N potassium hydroxide (NaOH optional), and (3) generate a schedule of acid and/or base additions to achieve desired pH endpoints for use in the RU-SR002.1 protocol. A detailed procedure for each part of the pretest follows.

8.1. Natural pH of Solid Materials

8.1.1. Place the minimum dry equivalent mass (i.e., 8 g dry sample) into an appropriate beaker. The equivalent mass of "as-received" material can be calculated if the solids content is known following Equation (A6-1).

$$M_{rec} = \frac{M_{dry}}{SC} \tag{A6-1}$$

where M_{rec} is the mass of the "as-received" material (g), M_{dry} is the dry equivalent sample mass [i.e., 8 g dry sample) (g dry)], and SC is the solids content of the material (g dry/g).

8.1.2. Using a graduated cylinder, measure out the appropriate volume of DI water based on a LS of 100 mL/g dry sample and add it to the beaker. Also, add a magnetic stirring bar to the beaker.

8.1.3. Agitate the slurry with a magnetic stirrer at medium speed for 5 min.

8.1.5. Make three pH measurements reading within 30 to 60 sec after the transfer and record the average.

8.1.6. Based on the mean natural pH value, determine if acid, base, or a combination of the two is required to cover the range of pH from 2 to 12. For example, if the material has a natural pH of 12.4 (e.g., a material treated by solidification/stabilization), then only acid would be needed. However, if a soil with a natural pH of 6.7 is to be tested, both reagents are required. Acid is used to lower the solution pH and base is used to raise the solution pH.

8.2. pH Titration

8.2.1. To the slurry formed in Section 8.1, add a minimum aliquot of 100 μL of 2 N nitric acid and mix for a minimum of 20 min at medium speed using a magnetic stirrer. In the case where only base is required to raise the solution pH, follow Steps 8.2.1 through 8.2.3 substituting "base" for "acid."

8.2.2. Allow the suspension to settle for 5 min and perform a pH measurement of the solution.

8.2.3. Record the cumulative volume of acid and the corresponding solution pH.

8.2.4. Repeat the process (Steps 8.2.1 and 8.2.3) using 100-μL increment additions of the 2 N acid, recording each addition and the subsequent pH measurement until the appropriate pH range is obtained. If it is anticipated that the material has a high amount of acid neutralization capacity, larger aliquots (e.g., 250 μL) may be added as long as the pH shift after completed mixing is less than three pH units.

8.2.5. If necessary, repeat Section 8.1 and Steps 8.2.1 through 8.2.4 using 1 N KOH solution to obtain a required pH range (typically between pH values of approximately 2 and 12).

9. Data Interpretation

The data from the pH001.0 protocol must be analyzed in terms of the solution pH resulting from the cumulative addition of equivalents of acid or base normalized for a gram of dry sample. The following example data (Table A6-1) which may result from this pretest using 2 N HNO_3 and 1 N KOH for a material with near-neutral natural pH and medium buffering capacity is used for illustrative purposes only. Equivalents and volumes of base are presented as negative values of acid (i.e., 1 mEq of base equals -1 mEq of acid and 1 mL of base equals -1 mL of acid). If the natural pH of the material is near or above 12.0, the pretest would result in data determined only by addition of HNO_3.

Using the solution pH response to cumulative acid and base addition, a material-specific titration curve similar to Fig. A6-1 can be generated for an LS ratio of 100 mL/g dry sample. Extrapolation of this titration curve to achieve target pH endpoints with other LS ratios (e.g., in SR002.1 protocol) will result in an approximate pH response.

9.1. SR002.1 Protocol Schedule

If a material-specific titration curve is not available, the "pH001.0 (pH Titration Pretest)" protocol must be conducted to determine the approximate equivalents of acid or base needed to achieve final pH end points for extractions ranging from pH 3 to pH 12. The required equivalents of acid or base are determined by creating a titration curve for the material, between these target pH values, and reading the equivalents from the curve that correspond to the target pH values. The pH response to acid and base additions as determined by this method will be approximate due to the large difference in LS ratio (i.e., LS of 100 mL/g dry for pH001.0 and LS of 10 mL/g dry for SR002.1).

Table A6-1.   Example pH 001.0 (pH Titration Pretest) results for a sample mass of 8 g dry sample.

Volume of 2 N HNO₃ or 1 N KOH Added (μL)	Equivalents of acid added [mEq/g]ᵃ	Solution pH
−6,400	−0.80	12.5
−4,800	−0.60	12.1
−4,000	−0.50	11.8
−3,200	−0.40	11.2
−2,400	−0.30	10.3
−1,600	−0.20	8.8
−800	−0.10	7.9
0	0.00	6.8
400	0.10	5.7
1,000	0.25	4.9
1,600	0.40	4.3
2,000	0.50	3.9
3,000	0.75	3.4
4,000	1.00	2.8
6,000	1.50	2.1

ᵃ2 N HNO₃ = 2 mEq/mL for the 8-g sample; therefore, 1,000 μL HNO₃ = 1 mL HNO₃ = 0.25 mEq HNO₃/g. Dry 1 N KOH = 1 mEq/mL for the 8-g sample; therefore, 1,000 μm KOH = 1 KOH = 0.125 mEq KOH/g.

9.1.1. Determine the equivalents of HNO₃ or KOH per dry gram of material required to reach all of the 11 desired end point pH values between 3 and 12 from the titration curve shown in Fig. A6-1. For each target pH, a horizontal line is drawn from the desired pH value to the titration curve. Then a vertical line is drawn from the titration curve to the equivalents of acid that are required to obtain this pH value. In this manner, the equivalents of acid or base required for all target end point pH values can be determined.

9.1.2. Convert the acid or base addition for each target pH from mEq/g dry sample to a volume addition of 2 N nitric acid or 1 N base using Equation (A6-2).
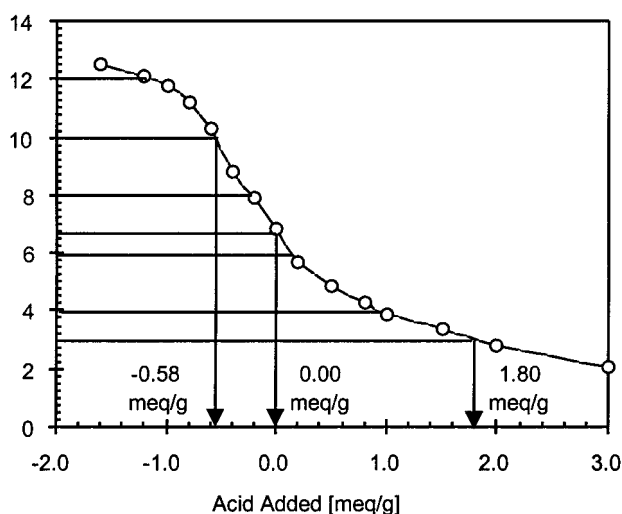

Figure A6-1.   Example "pH001.0 (pH Titration Pretest)" data showing schedule point selection for "SR002.1 (Alkalinity, Solubility and Release as a Function of pH)".

Table A6-2. Example schedule for acid addition for 40 g dry equivalent mass samples and a moisture content (dry basis) of 0.1 mL/g dry for the "SR002.1 (Alkalinity, Solubility and Release as a Function of pH)" protocol.

Extract no.	End point solution pH	Equivalents of acid to add (mEq/g)	Volume of 2 N HNO₃ or 1 N KOH (mL)	Volume of moisture in sample (mL)	Volume of DI water makeup (mL)
1	12.0	−1.10	44.0	4.0	352.0
2	11.0	−0.75	30.0	4.0	366.0
3	10.0	−0.58	23.2	4.0	372.8
4	9.0	−0.15	6.0	4.0	390.0
5	8.0	−0.09	3.6	4.0	392.4
6	Natural	0.00	0.0	4.0	396.0
7	6.0	0.08	1.6	4.0	394.4
8	5.0	0.12	2.4	4.0	393.6
9	4.0	0.90	18.0	4.0	378.0
10	3.0	1.80	36.0	4.0	360.0
11	2.0	3.10	62.0	4.0	334.0

$$V_{a/b} = \frac{A_{eq} \cdot M_{\mathrm{dry}}}{N_{a/b}} \tag{A6-2}$$

where $V_{a/b}$ is the volume of acid or base to be added (mL), A_{eq} is the amount of acid or base expressed in equivalents (mEq/g dry), M_{dry} is the dry equivalent sample mass (i.e., 8) (g dry), and $N_{a/b}$ is the normality of the acid (i.e., 2) or base (i.e., 1) (mEq/mL).

9.1.3. Calculate the volume of makeup DI water required to provide an LS of 10 mL of extractant per gram of dry solid sample. If the material has high moisture content, the volume of water contained within the sample should be subtracted from the total required leachant. For example, 40 g dry equivalent mass sample with a dry-basis moisture content of 10% (i.e., 0.1 mL/g dry) and requiring an addition of 15 mL of 2 N Nitric Acid would also require 381 mL of DI water as a makeup volume according to the following equation:

$$V_{DI} = (M_{\mathrm{dry}} \cdot LS) - V_{a/b} - (M_{\mathrm{dry}} \cdot MC_{\mathrm{d\ basis}}) \tag{A6-3}$$

where V_{DI} is the volume of DI water makeup (mL), M_{dry} is the mass of dry solid sample (i.e., 20) (g dry), LS is the test liquid to solid ratio (i.e., 10) (mL/g dry), $V_{a/b}$ is the volume of acid or base from the titration curve (mL), and $MC_{\mathrm{d\ basis}}$ is the moisture content on a dry mass basis (mL water/g dry) from ASTM D 2261-80.

Table A6-2 shows the example schedule of acid or base additions and DI water make up volume for the SR002.1 protocol generated from the titration information shown in Fig. A6-1 using 40 dry g of sample with a moisture content (dry basis) of 0.1 mL/g dry.

A.7. PS001.1 (PARTICLE SIZE REDUCTION)

1. Scope

1.1 This protocol is used to size reduce a solid material to a particle size of either <300 μm, <2 mm, or <5 mm for subsequent characterization.

2. Cited Protocols

2.1. ASTM (1980) "Standard Method for Water (Moisture) Content of Soil, Rock, and Soil–Aggregate Mixtures D 2261-80," Philadelphia, PA: American Society for Testing and Materials.

2.2. AW001.0 (Acid Washing of Laboratory Equipment).
2.3. SR002.1 (Alkalinity, Solubility and Release as a Function of pH).
2.4. SR003.1 (Solubility and Release as a Function of LS Ratio).

3. Summary of the Protocol

Depending on the nature of the solid samples, all solid samples to be subjected to equilibrium-based leaching protocols (e.g., SR00x.1 series protocols) must be particle size reduced to <300 μm, <2 mm, or <5 mm to minimize mass transfer rate limitation through larger particles.

Particle size reduction to 5 mm or 2 mm should be accomplished by crushing with a rock hammer in a thick (i.e., 4–8 mil), sealed plastic bag followed by sieving through either a 5 mm or 2 mm polyester sieve. Alternatively, a laboratory size jaw crusher can be used for particle size reduction to <2 mm or <5 mm.

Prior to particle size reduction to <300 μm, desiccation to a maximum moisture content of 15% (w/w) may be necessary for materials with naturally high moisture contents. Particle size reduction then is conducted in a closed vessel using a ball mill with an appropriate aggregate or other equivalent grinding apparatus (e.g., mortar and pestle or centrifugal grinder). Milling is immediately followed by separation of the <300 μm fraction through a 300-μm (50 mesh) sieve. The jar milling/sieving process is repeated on the fraction that does not pass the sieve until a minimum of 85% of the initial material mass has been size reduced and collected. The milled product is stored in an air-tight polyethylene vessel until required for leach testing.

4. Significance and Use

Large particle sizes may limit the release of constituents in extraction protocols used to measure constituent solubility or release at low liquid-to-solid (LS) ratios (i.e., SR002.1 and SR003.1). Testing protocols such as these are designed reach equilibrium between solid and liquid phases within reasonable test duration for material leaching characterization. Application of these protocols to materials of larger particle will necessitate longer contact time to obtain equilibrium between solid and liquid phases.

5. Apparatus

5.1. *Reduction Apparatus*—jar mill (e.g., U.S. Stoneware #764 AVM) with an appropriate grinding media (e.g., zirconia pellets, Fisher Scientific, or equivalent) or other apparatus suitable for size reducing solid materials.
5.2. *Mill Jar Vessel*—ceramic jar (e.g., Fisher Scientific #08-382C) or polyethylene bottle (e.g., Nalgene #2120-0005) with air-tight lid or equivalent.
5.3. *Rock Hammer*—e.g., Stanley Steelmaster SB24 or equivalent.
5.4. *Sealable Plastic Bag*—e.g., Ziploc Brand Freezer Bags, or equivalent.
5.5. *Jaw Crusher*—e.g., ASC Scientific Laboratory Size Jaw Crusher.
5.6. *Mortar*—e.g., Coors #60319, or equivalent.
5.7. *Pestle*—e.g., Coors #60320, or equivalent.
5.8. *Desiccator*—e.g., Fisherbrand #08-615B, or equivalent.
5.9. *Desiccant*—8 mesh indicating SiO_2 desiccant (e.g., EM Science, Gibbstown, NJ, or equivalent).
5.10. *Sieve*—5 mm high-density polyethylene U.S. standard sieve with polyester mesh.
5.11. *Sieve*—2 mm (10 mesh) high-density polyethylene U.S. standard sieve with polyester mesh (e.g., Cole Parmer #AP-06785-20, or equivalent).
5.12. *Sieve*—300 μm (50 mesh) stainless steel U.S. standard sieve with stainless steel mesh [A plastic body/mesh (e.g., polyethylene/polyester) is recommend if available at a 300 μm (50 mesh) opening.] (e.g., Fisherbrand #04-881-10T, or equivalent).
5.13. *Storage Vessel*—wide-mouth, polyethylene bottle with an air-tight lid (e.g., Nalgene #3120-9500, or equivalent).

6. Acid Washing Procedure

To minimize cross contamination of replicates or samples, all laboratory equipment that comes in contact with the material must be rinsed with 10% nitric acid followed by DI water to remove residual deposits following the "AW001.0

(Acid Washing of Laboratory Equipment)" protocol. For the "PS001.1 (Particle Size Reduction)" protocol, it is mandatory that equipment is acid washed between material types and recommended between replicates.

7. Particle Size Reduction Procedure

7.1. For particle size reduction to <5 mm or <2 mm, an initial mass of sample should be placed in a thick, sealable plastic bag on a hard surface.

7.2. With a rock hammer, crush the monolithic or large granular material into smaller units. If the integrity of the plastic bag is compromised during size reduction, the material may be transferred into a new bag.

7.3. As an alternative method, laboratory size jaw crusher can be used for particle size reduction to <5 mm or <2 mm.

7.4. When the material seems to be of a uniform particle size, sieve the material through a 5-mm sieve or a 2-mm sieve, retaining both the fraction that passes and the fraction that does not pass the sieve.

7.5. Return the fraction that does not pass the sieve into the plastic bag for continued size reduction.

7.6. Repeat Steps 7.2–7.4 until greater than 85% of the initial material mass has been reduced to either <5 mm or <2 mm. Place the entire sample mass into an air-tight vessel until a moisture content analysis is conducted.

7.7. Determine the moisture content of the material using ASTM method D 2261-80 "Standard Method for Laboratory Determination of Water (Moisture) Content of Soil, Rock, and Soil–Aggregate Mixtures."

7.8. For further particle size reduction to <300 μm, desiccation may be necessary if the moisture content of the material is greater than 15% (w/w). If no desiccation is required, continue particle size reduction with Step 7.8.

7.9. Place the solid material in a porcelain milling jar or plastic milling vessel that is approximately half filled with milling media. The total volume of media and sample should be less than 2/3 of the bottle volume.

7.10. Place the vessel on the ball mill and tumble it until the material breaks into smaller units. The duration of milling will vary depending on material properties. If the sample does not break down, grinding with a mortar and pestle followed by jar milling may be required.

7.11. Sieve the material through a 300-μm (50 mesh) sieve, collecting the particles that pass the sieve in an appropriate storage container.

7.12. Return the grinding media and the fraction that does not pass the sieve to the milling jar for additional particle size reduction. Alternately, continue to reduce the particle size using the mortar and pestle.

7.13. Repeat the milling/sieving process (Steps 7.9–7.12) until a minimum of 85% of the original mass has been particle size reduced to less than 300 μm.

7.14. Store the size-reduced material in an air-tight container to prevent contamination through exchange with the environment. Store in a cool, dark, and dry place until use.

A.8. AW001.0 (ACID WASHING OF LABORATORY EQUIPMENT)

1. Scope

1.1. This procedure is used to prepare laboratory equipment for use in inorganic extraction tests.

2. Summary of the Protocol

Because concentrations of inorganic constituents in leachates may be very low (i.e., <10 μg/L), all laboratory equipment that is exposed to the material, the extraction fluid, or the leachant must be rinsed with 10% nitric acid followed by DI water to remove residual deposits. This equipment includes supplies, utensils and containers or any surface that will come into direct contact with the material. After removing loose debris with soap and tap water, all contacting surfaces are rinsed with 10% nitric acid then triple rinsed with DI water. The equipment is dried and stored in such a manner as to minimize contamination with trace metals. When the equipment is used, no further preparation is required.

3. Reagents and Materials

3.1. *Cleaning Brush*—soft, nondamaging brush (e.g., Fisher Scientific, or equivalent).

3.2. *Detergent*—e.g., Sparkleen, Fisher Scientific, or equivalent.

3.3. *Reagent Grade Water*—DI water with a resistivity of 18.2 MO can be provided by commercially available deionization systems (e.g., Milli-Q Plus, Millipore, Bedford, MA, or equivalent).

3.4. *10% (v/v) Nitric Acid*—made by dilution of Tracemetal Grade nitric acid (e.g., Fisher Scientific, or equivalent) with DI water.

4. Acid Washing Procedure

4.1. Rinse loose debris from the surface of the object using tap water.

4.2. Wash the object thoroughly using a brush, soap, and water. Triple rinse with tap water.

4.3. Using a designated laboratory squirt bottle, apply a steady stream of 10% nitric acid solution to completely cover all contacting surfaces. Repeat the application of the 10% nitric acid three times.

4.4. Triple rinse all surfaces with DI water.

4.5. Dry the object by using direct sunlight, ovens, or forced drafts of warm air. Take care to limit exposure to airborne particulates or any source of contamination.

4.6. Objects that are not for immediately use must be covered or stored in an area where exposure to airborne particulates or any other source of contamination can be minimized. Alternately, all equipment can be triple dipped into a polyethylene crock (Cole-Parmer #AP-06724-60, or equivalent) containing a 10% nitric acid bath with a dipping basket (e.g., Cole-Parmer #AP-06717-50, or equivalent). For this approach, however, frequent monitoring of the metals concentration and renewal of the bath solution are required to minimize the possibility of depositing metals onto equipment surfaces.

5. Safety

Caution should be taken when working with either the full strength or 10% nitric acid solutions. At a minimum of safety precautions, the use of acid resistant gloves and eye protection are required. All equipment should be rinsed over a tank constructed of an inert material (e.g., polyethylene tank, Nalgene #14100-0015, or equivalent).